

PCT

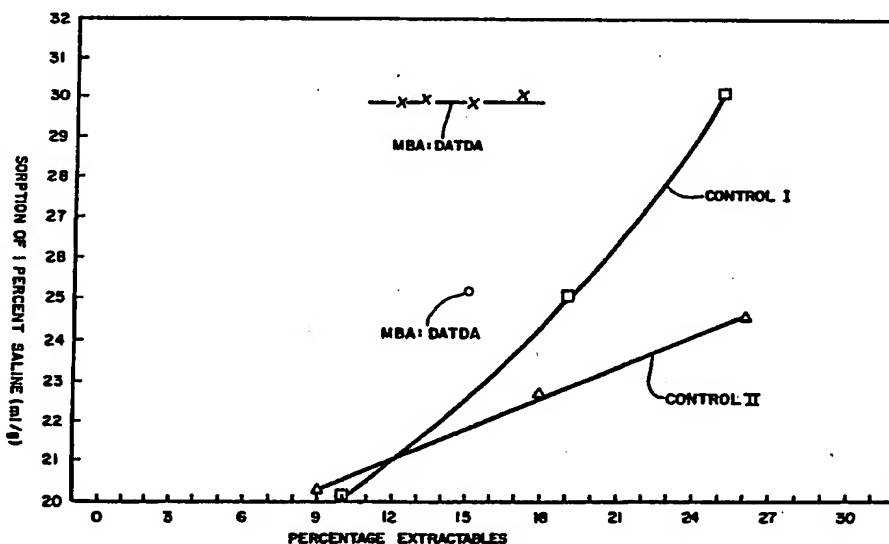
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C08F 226/02, 236/02, 236/22 B32B 27/00, 27/20, 27/38 D04H 1/64</p>	<p>A1</p>	<p>(11) International Publication Number: WO 90/15830 (43) International Publication Date: 27 December 1990 (27.12.90)</p>
<p>(21) International Application Number: PCT/US90/03304 (22) International Filing Date: 11 June 1990 (11.06.90) (30) Priority data: 365,224 12 June 1989 (12.06.89) US (71) Applicant: WEYERHAEUSER COMPANY [US/US]; 33663 Weyerhaeuser Way South, Federal Way, WA 98003 (US). (72) Inventors: KILIAN, Robert ; 79 Marion Road, Princeton, NJ 08540 (US). POCCIA, John ; 544 Sydney Avenue, Union Beach, NJ 07735 (US). REILLY, Eugene, P. ; 243 Glenn Avenue, Lawrenceville, NJ 08648 (US).</p>		<p>(74) Agents: GEIMER, Stephen, D.; Dressler, Goldsmith, Shore, Sutker & Milnamow, Ltd., 1800 Prudential Plaza, Chicago, IL 60601 (US) et al. (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (Euro- pean patent), JP, LU (European patent), NL (European patent), SE (European patent). Published With international search report.</p>

(54) Title: HYDROCOLLOID POLYMER



(57) Abstract

A water-swellaible hydrocolloid polymer is disclosed as are its uses in sorbent articles. The polymer consists essentially of about 80 to about 99.995 mole percent polymerized water-soluble alpha, beta-monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain, zero to about 19.995 mole percent polymerized water-soluble copolymerized monoethylenically unsaturated monomer, and about 0.005 to about 0.10 mole percent polymerized water-soluble copolymerizable cross-linker mixture. The cross-linker mixture consists essentially of a first and second cross-linker that are present relative to each other at about a 1:1.5 to about a 1:15 mole ratio. The first cross-linker is a bis- or tris-acryloyl-containing molecule, whereas the second cross-linker is a bis-allyl ether, amide, amine or triallylamine.

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TC	Togo
DK	Denmark			US	United States of America

-1-

HYDROCOLLOID POLYMER

DescriptionTechnical Field

5 The present invention relates to a water-swella-
ble cross-linked polymer frequently referred to as a hydrocolloid. More particularly,
the invention relates to a water-swella-
ble hydrocolloid polymer that is cross-linked by a
mixture of cross-linking agents whose use provides a
10 polymer that exhibits a smaller amount of
water-extractable solids at a given water sorbency
than does a similar polymer prepared from an equal
amount of any single cross-linker of the mixture when
used alone.

15 Background Art

Water-swella-
ble hydrocolloids are a well known class of materials that are sometimes also
referred to as hydrogels or superabsorbents. Such
polymers are frequently utilized in their dry or
20 semi-dry forms (e.g. 5-15 weight percent water) in
surgical dressings, disposable diapers, sanitary
napkins, incontinent pads, wipes, and the like. In
water-swollen form, hydrocolloids are often utilized
as contact lenses, as thickeners for foods and as
25 adhesives.

When used in dry or semi-dry form, utility
is made of the water sorbing (absorbing and/or
adsorbing) characteristics of the polymers. These
polymers can frequently sorb several hundred to about
30 1000 or more times their own weight of deionized or
distilled water.

Exemplary totally synthetic polymers are
typically prepared using about 50 to 99 or more mole
percent hydrophilic monomers such as
35 monoethylenically unsaturated carboxylic acids,

-2-

amides, hydroxyalkylene amides and esters, sulfonic acids, and phosphoric acids. The remainder of the monomers typically are copolymerizable alkyl esters or amides of monoethylenically unsaturated acids or nitrile-containing monomers such as acrylonitrile or methacrylonitrile. Totally synthetic hydrocolloids supplied in dry or semi-dry form typically contain about 50 to 99 or more mole percent polymerized monoethylenically unsaturated monocarboxylic acid, usually acrylic acid.

Such polymers are also usually cross-linked by a polyethylenically unsaturated monomer that is present in an amount of about 5 to about 0.001 mole percent of the total monomer mixture. Exemplary cross-linking monomers have acryloyl or allylic unsaturation, or a mixture thereof in one molecule as are exemplified by N,N'-methylenebisacrylamide or diethyleneglycol dimethacrylate, diallylamine, and allyl methacrylate or N,N-diallyl methacrylamide.

Hydrocolloid polymers are also known that are polysaccharides, e.g., modified cellulose and starches. Such modified polymers typically contain one to a plurality of hydroxyalkylene, amine, ammonium or carboxyalkylene groups per anhydroglucose repeating unit. These modified natural polymers can also contain cross-links in addition to those that may be present in the natural polymer.

Still further hydrocolloid polymers are prepared by grafting a synthetic polymer on to the backbone provided by a starch or cellulosic molecule. The grafted synthetic polymer portions are typically similar to those described before, but those grafted polymers typically are not cross-linked, or contain relatively more repeating units between cross-links than do the totally synthetic polymers.

-3-

Exemplary totally synthetic carboxy-functional hydrocolloids are described in U.S. Patents No. 2,247,171; No. 2,798,053; No. 2,810,716; No. 3,247,171; No. 3,229,769; 5 No. 3,686,024; No. 3,872,063; No. 4,062,817; No. 4,066,583; No. 4,167,464; No. 4,178,221; No. 4,192,727; No. 4,248,685; No. 4,308,148; No. 4,654,039 and in PCT/US 80/01567 (WO 81/01850).

Modified starch and cellulose derivatives 10 are exemplified by carboxymethyl cellulose and hydroxyethyl cellulose that are commercially available from several sources. A cross-linked carboxymethyl cellulose is described in U.S. Patent No. 2,639,239.

15 Grafted starch and cellulose derivatives are described in U.S. Patents No. 3,635,857; No. 3,640,826; No. 4,028,290; No. 4,076,663; No. 4,105,033; and No. 4,340,057.

Although modified and grafted 20 polysaccharides can provide adequate hydrocolloid materials, such materials typically require several steps to prepare in addition to those required for totally synthetic hydrocolloids and are thus energy and labor intensive to prepare as compared to totally 25 synthetic hydrocolloids. Thus, the totally synthetic hydrocolloid polymers are preferred herein on a cost and energy basis.

Of the various types of hydrocolloid, e.g., totally synthetic, modified polysaccharide or grafted 30 polysaccharide, some are soluble or dispersible in water to the extent that a viscosity can be measured, whereas other hydrocolloids are substantially not so soluble or dispersible in water. Such solubilities or dispersibilities are frequently determined in 35 distilled or deionized water, or sometimes in one

-4-

normal sodium chloride or in synthetic urine solutions.

Hydrocolloids that are substantially soluble or dispersible in aqueous solutions can provide products whose hydrocolloid polymer is extracted by contact with aqueous solutions such as urine when used in a diaper, or blood or lymph when used as a wound dressing, and thereby can provide an unpleasant feel or a contaminant, respectively. In addition, U.S. Patent No. 4,654,039 theorizes that such leaching of soluble hydrocolloid from a sorbing article of manufacture such as a diaper by a body fluid such as urine can alter both the chemical and physical characteristics of the body fluid to the extent that the fluid is more slowly absorbed and more poorly held by the hydrogel-containing sorbent article. Such a situation can contribute to undesirable leakage of body fluid from the sorbent article. A similar problem as to water-extractables is noted in U.S. Patent No. 4,286,082.

For a totally synthetic hydrocolloid, a trade-off between sorbing power of the polymer material (absorbancy) and the amount of fluid-extractable material usually results. Thus, the amount of fluid-extractables can be diminished by increasing the amount of cross-linker used during polymerization, but that increase in cross-linker also typically leads to a decrease in the amount of body fluid that can be sorbed by hydrocolloid.

U.S. Patent No. 4,286,082 teaches that hydrocolloid polymers can be prepared that exhibit a relatively high absorbency of one molar sodium chloride solution and a relatively high initial water sorption rate. Such hydrocolloid polymers are said to be obtained by polymerization of an aqueous

-5-

admixture containing 100 parts by weight of an acrylate salt monomer composed of zero to 50 mole percent of acrylic acid and 50 to 100 mole percent of an alkali metal acrylate, and 0.001 to 5 parts by weight of a copolymerizable cross-linkable monomer containing two to four acryloyl, methacryloyl or allyl groups in the molecule in the presence of at least one surface-active agent selected from the group consisting of water-soluble and water-dispersible surface-active agents in the presence of a water-soluble radical polymerization initiator. The polymerization is said to be carried out at a concentration range of from 25 weight percent through saturation. The surface-active agent is utilized at a concentration of 0.1 to 10 parts by weight, preferably 0.05 to 5 parts by weight, and more preferably 0.1 to 2 parts by weight, per 100 parts by weight of the acrylate salt monomer. The polymer is dried and then pulverized for use.

The useful surface-active agents are said to be both non-ionic and anionic. Non-ionic surface-active agents having an HLB of 7 to 20 and preferably 8 to 17 are said to be desirable.

U.S. Patent No. 4,654,039 teaches that relatively high absorptions of a body fluid exemplified by a synthetic urine solution can be achieved, while maintaining relatively low amounts of synthetic urine-extractable material, by use of a particular method of polymerization. In accordance with that method, a reaction mixture is prepared in an aqueous medium that consists essentially of from about 5 to 35 percent by weight of acid group-containing monomers in the free acid form, from about 0.001 mole percent to 5 mole percent of the cross-linking agent based on total monomers used, and

-6-

from zero to about 5 mole percent of a free radical initiator based on total monomers used. The reaction mixture is substantially free of graft polymerizable polymer moieties such as starch or cellulose. The
5 reaction mixture is thereafter subjected to polymerization conditions that are sufficient to produce, after partial neutralization, a polymer with the desired characteristics of swell, sheer modulus when swollen, and extractables.

10 The polymer that ultimately results is said to be a substantially water-insoluble, slightly cross-linked, partially neutralized, hydrogel-forming material. The polymer is said to consist essentially of from about 50 to 99.999 mole percent polymerized
15 unsaturated polymerizable acid group-containing monomers and from about 0.001 to 5 mole percent of a polymerized cross-linking agent. The polymer has a degree of neutralization of at least about 25 percent and is substantially free of graft polymerized
20 polymer moieties such as starch or cellulose.

The polymer composition of U.S. Patent No. 4,654,039, upon neutralization to a degree of neutralization of at least about 50 percent, is said to have or would have a gel volume of at least about
25 20 grams of synthetic urine per gram of polymer, a sheer modulus of the hydrogel of at least about 2000 dynes/cm², an initial extractable polymer content of no more than about 7.5 weight percent (after one hour in the synthetic urine) and an equilibrium
30 synthetic urine-extractable polymer content of no more than about 17 weight percent.

U.S. Patent No. 4,654,039 goes on to teach that its hydrogel-forming polymer materials must be prepared primarily from the acid group-containing
35 monomers disclosed. That patent further teaches that

-7-

substantially all of the unsaturated acid group-containing monomers in the aqueous reaction mixture must be polymerized in their free acid, unneutralized form. That method of polymerization is said to differ from those taught in U.S. Patents No. 4,286,082 and No. 4,340,706 wherein mixtures of free acid monomers and their salts are utilized. Acrylic acid is an especially preferred acid group containing monomer.

Several types of cross-linking agents are said to be useful in preparing the hydrogel-forming polymers of U.S. Patent No. 4,654,039. Suitable cross-linkers are said to include, (1) compounds having at least two polymerizable double bonds; (2) compounds having at least one polymerizable double bond and at least one functional group reactive with the acid-containing monomer material; (3) compounds having at least two functional groups reactive with the acid-containing monomer material; and (4) polyvalent metal compounds that can form ionic cross-linkages. A long list of useful cross-linking agents of group (1), above, is provided in that patent that includes polyvinyl compounds, polyacryloyl esters, bisacrylamides, polyallylically unsaturated ethers, esters and amines, and compounds having both acryloyl and allylic unsaturation.

There is no teaching, however, of mixing cross-linking agents, nor more specifically, of mixing cross-linking molecules that have only acryloyl and only allylic unsaturation as is disclosed hereinafter. There is also no teaching of which the inventors herein are aware that a cross-linking mixture such as that described hereinafter would be useful in the preparation of a hydrocolloid polymer, nor that use of such a mixture

-8-

of cross-linkers might provide any advantage over the use of one of the cross-linkers alone.

Although the teachings of U.S. Patent No. 4,654,039 appear to indicate success in the preparation of hydrocolloid polymers, some of the examples of that patent; i.e., Examples, X, XII, and XVI, appear to indicate that relatively high amounts of extractables (e.g., 9, 13, and 11 percents, respectively) are still produced at relatively low concentrations (e.g., 0.02, 0.02, and 0.03 mole percents, respectively) of the single cross-linking agent there used, methylenebisacrylamide. In addition, the method of preparing a hydrogel of that patent requires that the polymer be polymerized as the free acid that is thereafter partially neutralized.

It would be beneficial if hydrocolloid polymers could be prepared that exhibited relatively high absorbency combined with relatively low amounts of extractables using relatively low amounts of cross-linking agent. It would also be beneficial if such hydrocolloid polymers could be prepared in a state of acid group neutralization that is substantially that at which the hydrocolloid is to be used so that the subsequent neutralization step described in U.S. Patent No. 4,654,039 could be avoided.

Brief Summary of the Invention

The present invention contemplates a water-swellaible polymer and a sorbent polymer-coated web and their uses.

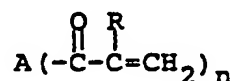
The water-swellaible polymer also referred to herein as a hydrocolloid polymer consists essentially of about 80 to about 99.995 mole percent polymerized

-9-

water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain, zero to about 19.995 mole percent polymerized water-soluble copolymerizable monoethylenically unsaturated monomer, and about 0.005 to about 0.10 mole percent polymerized water-soluble, copolymerizable cross-linker mixture based upon the total moles of copolymerizable monomer present. The monoethylenically unsaturated monomers contain about 5 to about 70 mole percent free acid and about 30 to about 95 mole percent acid neutralized with a water-soluble monovalent cation. The cross-linker mixture consists essentially of a first and a second cross-linker that are present at a mole ratio to each other of about 1:1.5 to about 1:15 in the order recited.

The first cross-linker has a structure that corresponds to the formula:

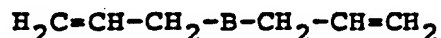
20



wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free from copolymerizable unsaturation and that is terminated by oxygen or nitrogen atoms; i.e., A is

bonded to each $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\overset{\text{R}}{\mid}}{\text{C}}=\text{CH}_2$ (acryloyl) group through an oxygen or nitrogen atom.

The second cross-linker has a structure that corresponds to the formula:



35

-10-

wherein B is a divalent radical that is an allylimino radical or contains a chain of 2 to about 10 atoms free from copolymerizable unsaturation and that is terminated by oxygen or nitrogen atoms; i.e.,
5 B is bonded to each $H_2C=CH-CH_2-$ (allyl) group through an oxygen or nitrogen atom.

When 60 mole percent of the polymerized acid groups are neutralized, the polymer sorbs 600 to about 1200 milliliters of deionized water per dry gram
10 of polymer. The polymer, after such sorbing, exhibits less than about 45 weight percent extractables, as is described hereinafter.

The polymer preferably contains only the polymerized monocarboxy monomer and polymerized
15 cross-linker mixture. The monocarboxy monomer is preferably partially neutralized acrylic acid. The first cross-linker is preferably methylenelbisacrylamide, whereas the second cross-linker is preferably diallyl tartardiamide.

Another aspect of the present invention
20 contemplates a polymer-coated web or sorbent layer that is useful in sorbent products such as diapers, incontinent pads, tampons and the like. The sorbent layer constitutes a water-insoluble fibrous web
25 matrix that contains a coating of the before-described hydrocolloid polymer that is present at about 2000 to about 1500 percent of the weight of the fibrous web matrix. The fibrous web matrix has a dry bulk recovery of at least about 30 percent, an
30 initial dry bulk of at least about 20 cc/g, and a weight of less than 2 ounces per yard (oz/yd).

A sorbent layer such as is described above is preferably prepared by submerging the fibrous web
matrix into an aqueous solution of the monomers and
35 cross-linker mixture present at a solids level of

-11-

about 55 to about 70 weight percent, removing the wet matrix and polymerizing the monomers and cross-linkers by electron beam irradiation. The sorbent web is thereafter dried. In particularly preferred practice, the sorbent layer is compressed to at least about 50 percent of its thickness prior to drying and maintained at least about 50 percent of its thickness during the drying to provide a compressed sorbent layer.

Brief Description of the Drawings

In the drawings forming a portion of this disclosure:

Figure 1 is a graph that illustrates sorption of deionized water in milliliters per gram (ml/g) of a series of polymers. The polymers were prepared from an aqueous solution containing 60 mole percent neutralized acrylic acid monomer and various mole percentages of water-soluble cross-linking agents, based upon the moles of total acrylic acid/acrylate salt present. The monomer/cross-linker solutions contained about 65 weight percent solids. The monomers and cross-linkers were polymerized by a single electron beam irradiation at a dose of 2 megarads (Mrads). The water-soluble cross-linkers were as follows: DATDA (X) = diallyl tartardiamide; PEG (N = 9) (□) = polyethylene glycol (9) diacrylate; MBA (△) = methylenebisacrylamide; and TMPTA (+) = trimethylolpropane triacrylate. Sorptions of deionized water were determined as described in the Materials and Methods Section.

Figure 2 is a graph that illustrates data for sorption of deionized water, as in Figure 1, versus percentage extractables for polymers similar to those of Figure 1 containing 0.01, 0.03 and 0.05

-12-

mole percent DATDA(+), and 0.01, 0.03 and 0.05 mole percent MBA (□). Data for a hydrocolloid polymer controls (O) are also shown. The control polymers samples were prepared from aqueous solutions containing 60 percent neutralized acrylic acid and no cross-linker at 65 weight percent solids. The datum point at the far right for the control polymer was obtained for a polymer irradiated with a 2 Mrad dose. The polymer of the center datum point was irradiated twice with a 2 Mrad dose, whereas the polymer of the far left datum point was irradiated three-times with a 2 Mrad dose. Percentage extractables and sorption assays are discussed hereinafter in the Materials and Methods section.

Figures 3 and 4 are graphs that illustrate sorption of deionized water and one percent saline (sodium chloride), respectively, versus the percentage of MBA in mixed MBA/DATDA cross-linked hydrocolloid polymers. The polymers were prepared using a single 2 Mrad irradiation dose flux on an aqueous composition containing 60 mole percent neutralized acrylic acid monomer plus a total of either 0.03 or 0.05 mole percent (Total Mole %) cross-linkers, based upon the partially neutralized acrylic acid monomer. Results for polymers containing 0.03 mole percent total cross-linker are shown as a solid line, whereas those for 0.05 mole percent total cross-linker are shown as a dashed line. Sorption data were obtained as discussed in the Materials and Methods section.

Figure 5 is a graph that is identical to the graph of Figure 2 with two additional datum points obtained from hydrocolloid polymers prepared utilizing a mixed pair of cross-linkers in accordance with this invention. The two added datum points are

-13-

for a hydrocolloid polymers prepared from aqueous solutions of 60 percent neutralized acrylic acid plus a total of 0.05 mole percent mixed cross-linker that contained about 65 weight percent solids and were irradiated with a single dose of 2 Mrads. As shown, one of those polymers contained a mixture of MBA and DATDA at a 0.01:0.04 mole ratio, whereas the second polymer contained those monomers at a 0.02:0.03 mole ratio, in the order named.

Figure 6 is a graph that illustrates sorption of 1 percent saline versus the percentage extractables for a series of hydrocolloid polymer-coated web matrices (sorbent layers) of the invention and two sets of control sorbent layers. The hydrocolloid polymers of all sorbent layers were prepared from 60 mole percent neutralized acrylic acid present in an aqueous solution at about 65 weight percent solids. The aqueous monomer-containing solution for the sorbent layers of the invention also contained mixtures of cross-linkers (MBA and DATDA). One group of sorbent layers of the invention (MBA:DATDA; X) was prepared with MBA:DATDA mole ratios of 0.01:0.04, 0.01:0.4; 0.01:0.06 and 0.005:0.06 (left to right), whereas the single datum point (MBA:DATDA; O) utilized a mole ratio of 0.02:0.03. The two sorbent layers of the invention and one control sorbent layer (Control I; \square) utilized a 5.5:1 weight add-on of polymer to web matrix. The second control sorbent layer (Control II, \triangle) utilized a 10:1 weight add-on of polymer to web matrix. Further details concerning the data and polymerizations are found in the Materials and Methods section.

Figure 7 is a graph that illustrates sorption of 1 percent saline versus residual monomer

-14-

(as acrylic acid or acrylic ester dimer) in parts per million (ppm) for three sorbent layers of the invention of Figure 6 (MBA:DATDA; X) and two control sorbent layers (Control; O). Weight add-ons of 5.5:1 of hydrocolloid polymer to web matrix were used. Further details concerning the data and polymerizations are found in the Materials and Methods section.

The present invention provides several benefits and advantages.

One benefit is that hydrocolloid polymers having relatively high absorbancy levels and relatively low amounts of extractables can be prepared.

Another benefit of the invention is that hydrocolloid polymers having desired absorbancy and extractables characteristics can be prepared at a level of acid group neutralization that is substantially that at which the hydrocolloid is ultimately utilized.

An advantage of the present invention is that its hydrocolloid polymers can be utilized in a particulate state dispersed in other materials into sorbent products such as diapers, sanitary napkins, surgical or wound dressings, wipes and the like.

A still further advantage of the present invention is that its polymerizations permit a hydrocolloid to be formed onto a supporting fibrous web that can later be incorporated into sorbent products such as those described above.

Still further benefits and advantages of the invention will be apparent to those skilled in the art from the disclosure that follows.

-15-

Detailed Description of the Invention

The present invention contemplates a water-swellaible polymer. That polymer consists essentially of about 80 to about 99.995 mole percent

5 polymerized water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain, zero to about 19.995 mole percent polymerized water-soluble, copolymerizable monoethylenically unsaturated

10 monomer, and about 0.005 to about 0.10 mole percent polymerized water-soluble, copolymerizable cross-linker mixture. The cross-linker mixture consists essentially of a first and a second cross-linker that are present at a mole ratio to each

15 other of about 1:1.5 to about 1:15 in the order recited. The first cross-linker has a structure that corresponds to the formula:



wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free

25 from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms.

The second cross-linker has a structure that corresponds to the formula:



wherein B is a divalent radical that is an allylimino radical or contains a chain of 2 to about 10 atoms free from copolymerizable unsaturation that

35 is terminated by oxygen or nitrogen atoms.

-16-

When neutralized with potassium or sodium hydroxide in an amount sufficient to neutralize about 60 mole percent of the polymerized acid group-containing monomers present, the polymer sorbs
5 about 600 to about 1200 mililiters of deionized or distilled water per dry gram of polymer, and exhibits less than about 45 weight percent extractables after sorbing that deionized or distilled water. The polymer is preferably substantially free of
10 surface-active agents, although such materials can be present.

The hydrocolloid polymers of the present invention are described in terms of the composition of monomers utilized in their preparation. They are
15 thus referred to as containing various "polymerized" monomeric species. In many instances, the characterization of a polymer on the basis of the monomers used in its preparation can be inaccurate because of the presence of relatively large amounts
20 of unreacted monomers. Here, however, it is believed that a characterization of the polymerized hydrocolloid based upon the monomer mixture used for its preparation is accurate because of subsequent analyses that indicate a relatively low level of
25 residual monomers in the dried hydrocolloid materials.

The principal monomeric constituent of a hydrocolloid of this invention is an alpha,beta-monoethylenically unsaturated monocarboxy compound containing a three carbon atom chain.

30 The phrase "monocarboxy monomer" is utilized herein to mean a monomer that contains a single carboxy functionality. That single carboxy functionality is itself a mixture of the free acid and monovalent cation salt forms of the free acid, as
35 is discussed in further detail hereinafter. The

-17-

phrase "monocarboxy monomer" is thus used herein as a short-hand phrase for the partially neutralized mixture of free acid and salt forms of the alpha,beta-monoethylenically unsaturated monocarboxy monomer.

The monocarboxy monomer and all of the other monomeric species discussed herein are referred to as being "water-soluble". That phrase is utilized herein to mean that whatever monomeric species is discussed is soluble in the aqueous mixture of monomeric species used for polymerization at the concentration utilized herein. To that end, the monocarboxy monomer and other monomers form clear, as compared to translucent or opaque, solutions in the aqueous monomer mixture at the concentration of use. Put differently, a water-soluble monomer forms a single phase when admixed with any other monomers and cross-linker mixture in water at the concentration at which that monomer is utilized herein.

Exemplary monocarboxy monomers useful herein contain a chain of three carbon atoms including the vinyl group, and are exemplified by acrylic acid, methacrylic acid and cyanoacrylic acid. Mixtures of these monocarboxy monomers can also be used. Acrylic acid is particularly preferred where an electron beam polymerization method is used, whereas methacrylic acid is preferred where a water-soluble free radical-initiated polymerization is utilized as a polymerization initiator.

The monocarboxy monomer constitutes about 80 to about 99.995 mole percent of the prepolymerized monomeric mixture and polymerized monomers. More preferably, that monomer is present at about 95 to about 99.995 mole percent, and most preferably, only the monocarboxy monomer and the mixture of

-18-

cross-linking agents are present in the monomer mixture and in the polymerized hydrocolloid.

As noted earlier, the monocarboxy monomer is itself a mixture of free acid and monovalent cation salt forms. The monovalent cation salt is formed from an alkali metal or monoamine. Alkali metal salts are preferred, with sodium and potassium salts being particularly preferred. Ammonium salts prepared from ammonia and monoamines are also useful but are preferably salts of sterically hindered, non-nucleophilic primary or secondary amines or, more preferably, tertiary amines such as tri-C₁-C₄ alkyl amines such as trimethylamine, triethylamine and tributylamine, or tri-C₂-C₃ alkanolamines such as triethanolamine and tri-isopropanol amine.

Polyvalent cation salts of the monocarboxy monomers are not utilized and are thus substantially absent from the monomer mixture and polymerized hydrocolloid. Polyvalent metal ions such as calcium, magnesium, aluminum and iron and polyvalent ammonium salts such as N,N,N',N'-tetramethylethylenediamine can cross-link the monomer mixture and resulting polymerized hydrocolloid.

The free acid form of the monocarboxy monomer typically constitutes about 5 to about 70 mole percent of the monocarboxy monomer mixture, and more preferably constitutes about 10 to about 40 mole percent. The monovalent cation salt therefore constitutes about 95 to about 30 mole percent, and more preferably about 90 to about 60 mole percent of the monocarboxy monomer. The alpha,beta-monoethylenically unsaturated monocarboxy monomer is thus partially neutralized, with the amount of acid group neutralization being about 30 to about 95 mole percent, and more preferably about 60 to about 90 mole percent.

-19-

Use of a partially neutralized alpha, beta-monoethylenically unsaturated monocarboxy monomer saves the subsequent step of neutralization after polymerization, which step can be somewhat
5 difficult to carry out to the gelatinous nature of aqueous compositions of the polymerized material. In addition, polymerization of a partially neutralized monocarboxy monomer whose degree of neutralization is substantially that desired in a sorbent product
10 facilitates the preparation of hydrocolloid polymer-coated webs (sorbent layers) for use in such products inasmuch as such webs are typically somewhat more difficult to manipulate than is the polymerized hydrocolloid itself.

15 One or more additional copolymerizable, water-soluble monoethylenically unsaturated monomers can also be present in the monomer mixture and polymerized hydrocolloid. Such monomers are familiar to those skilled in the hydrocolloid art and include
20 methacrylamide, acrylamide, N-mono- and N,N-di-C₁-C₄ alkyl acrylamides and methacrylamides such as N-methyl acrylamide, and N,N-dipropyl methacrylamide, C₂-C₃ 2-hydroxyalkyl acrylamides and methacrylamides such as N-(2-hydroxy)propyl
25 acrylamide and N,N-di(2-hydroxy)ethyl methacrylamide, methyl acrylate and methacrylate, C₂-C₃ 2-hydroxyalkyl acrylate and methacrylate, acrylonitrile and the like. The additional co-polymerizable, water-soluble monoethylenically
30 unsaturated monomers can also include acid-functional monomers and their water-soluble monovalent cation salts. Included among these monomers are crotonic acid, itaconic acid, maleic acid, maleic anhydride (which readily hydrolyzes to the acid), C₁-C₆
35 N-alkyl monoamides of maleic acid, the C₂-C₃

-20-

N-(2-hydroxy)alkyl and N,N-di-(2-hydroxy)alkyl monoamides of maleic acid, sulfonic acid compounds such as styrenesulfonic acid, 2-vinyl-4-ethylbenzenesulfonic acid, 2-sulfoethylmethacrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, and vinylsulfonic acid, and phosphate-containing monomers such as methacryloxy ethyl phosphate.

A copolymerizable monoethylenically unsaturated monomer or a mixture thereof can be present at zero to about 19.995 mole percent of the monomer mixture and polymerized hydrocolloid. More preferably, such monomer or monomers is present at about 5 to about 10 mole percent. Most preferably, the copolymerizable monoethylenically unsaturated monomer is absent.

When present, the copolymerizable monoethylenically unsaturated monomer is preferably selected from the group consisting of acrylamide, methacrylamide, N-2-hydroxyethyl acrylamide, N-2-hydroxyethyl methacrylamide, styrene sulfonic acid, 2-sulfoethylmethacrylic acid, and 2-acrylamido-2-methylpropanesulfonic acid.

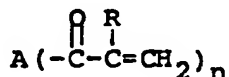
Inasmuch as an aqueous solution of the above-mentioned copolymerizable acid-functional monoethylenically unsaturated monomer and previously discussed monocarboxy monomer equilibrates rapidly to distribute the monovalent cations among the acid groups that are present in accordance with the pK_a values of the various acid groups and the pH value of the solution, admixture of the free acid form of one monomer and a salt form of that or another monomer provides a complex admixture in which it is not possible to ascertain which cation or proton originated from any given monomer. Consequently, the before-mentioned degree of partial acid group

-21-

neutralization is to be understood to be the degree of neutralization of all of the acid groups present in the monomer mixture and resulting, polymerized hydrocolloid when acid-functional monomers in addition to the monocarboxy monomer are present in the monomer mixture or in polymerized form. Since the monocarboxy monomer and the additional copolymerizable monomers that can be present are monoethylenically unsaturated, the degree of neutralization of all of the acid group-containing monomers can be referred to in terms the neutralization of monoethylenically unsaturated monomers.

The third element of a monomer mixture and resulting polymer of this invention is a mixture of copolymerizable, water-soluble cross-linking agents or cross-linkers. The mixture of cross-linkers consists essentially of a first cross-linker and a second cross-linker that are present at a mole ratio to each other of about 1:1.5 to about 1:15, more preferably at about 1:4 to about 1:10, and most preferably at a mole ratio of about 1:5 to about 1:7.

The first cross-linker can be described as a bis- or tris-acryloyl compound and has a structure that corresponds to the formula:

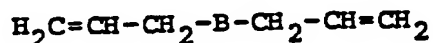


wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms. The A radical is preferably divalent; i.e., n is preferably 2.

-22-

The second cross-linker is triallylamine (discussed separately hereinafter) or can be described as a bis-allyl compound and has a structure that corresponds to the formula:

5



wherein B is a divalent radical that is an allylimino radical or contains a chain of 4 to about 10 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms; i.e., B is bonded to each allyl group through an oxygen or nitrogen atom.

Divalent and trivalent radicals A and B above, while generally being different in structure, share the properties of "containing a chain of 3 (or 4) to about 30 (or 10) atoms" being "free from copolymerizable unsaturation" and being "terminated by oxygen or nitrogen atoms." These phrases are utilized herein as follows.

The phrase "free from copolymerizable unsaturation" is used to mean that although some unsaturation can be present in either radical, that unsaturation does not take part in a polymerization reaction contemplated herein. Exemplary of such unsaturation is that found in a benzene ring.

The phrase "contains a chain of 3 (or 4) to about 30 (or 10) atoms" is meant to indicate a lower limit of chain length of 3 or 4 atoms in a straight or branched chain radical whose longest axis contains at least 3 or 4 atoms, respectively, and is the axis that joins the two or three acryloyl or allylic portions of the molecule, and which axis can be as long as 30 or 10 atoms, respectively. The enumerated number of atoms in the phrase is also meant to encompass the presence of one or more rings whose axial length between the two or three acryloyl or

-23-

allylic portions of the molecule cannot be defined in terms of whole numbers of atoms. The phrase is still further intended to encompass the terminal oxygen or nitrogen atoms, that are discussed below.

5 The phrase "terminated by oxygen or nitrogen atoms" is meant to indicate that the two or three acryloyl portions of the first cross-linker are present as esters or amides, respectively, whereas the two allyl portions can be present as ethers
10 (oxygen atom-terminated), or amides, or amines (nitrogen atom-terminated), respectively. Thus, where A or B is cyclic and may therefore not strictly speaking contain termini, such cyclic radicals are considered herein to have termini that are defined by
15 the atoms that bond the A or B radicals to the acryloyl or allylic portions. The phrase is also meant to indicate that the terminal atoms of the divalent or trivalent radicals are the same atom, which can be either oxygen or nitrogen. Thus, the
20 first cross-linker is, for example, a tris- or bis-acrylate, a tris- or bis-methacrylate, a tris- or bis-acrylamide or a tris- or bis-methacrylamide. The water-soluble allyl derivatives that constitute the second cross-linker are bis-compounds, except for
25 triallyl amine as is discussed hereinafter.

Exemplary useful water-soluble first cross-linkers formed from a preferred divalent A radical include methylenebisacrylamide, methylenebismethacrylamide,
30 trimethylenebisacrylamide, a polyethylene glycol (PEG) diacrylate or methacrylate that contains an average of one to about 9 PEG units per molecule such as ethyleneglycol dimethacrylate, tetraethyleneglycol diacrylate [that can also be named polyoxyethylene
35 (4) diacrylate or PEG-4 diacrylate], and

-24-

polyoxyethylene (9) diacrylate [that can also be
named nonaethyleneglycol diacrylate or
polyethyleneglycol (9) diacrylate], meta-xylylenyl
bisacrylamide (the bisamide formed between two moles
5 of acrylic acid and one mole of
meta-xylylenediamine), 1,6-hexanediol diacrylate,
1,4-butanediol diacrylate, 1,3-butanediol diacrylate,
and the like. Exemplary tris-acrylates and
methacrylates include trimethylolpropane triacrylate
10 (TMPTA) and trimethacrylate, respectively, as well as
pentaerythritol triacrylate or trimethacrylate.

Of the above first cross-linkers,
methylenebisacrylamide (MBA) and PEG diacrylates
containing an average of 1 to 9 PEG units per
15 molecule are preferred, with MBA being particularly
preferred.

Exemplary useful second cross-linkers
include water-soluble di- or bisamides of an
allylamine and dicarboxylic acids such as those
20 formed from carbonic acid, oxalic acid, malonic acid,
succinic acid, malic acid and tartaric acid, which
can be named diallyl urea, diallyl oxaldiamide,
diallyl malondiamide, diallyl succindiamide, diallyl
malldiamide and diallyl tartardiamide. Exemplary
25 diallyl diamines include N,N'-diallylpyperazine,
N,N'-diallylethylenediamine and the like.

Also included in the second group are di- or
bis-ethers of an allyl alcohol and a polyhydric
alcohol (polyol) having a chain length of 2 to about
30 10 atoms. Exemplary diethers include the
polyethylene glycol (PEG) derivatives that include an
average of 1 to 3 PEG repeating units per molecule
such as ethyleneglycol diallyl ether,
diethyleneglycol diallyl ether and triethyleneglycol
35 diallyl ether. Further diallyl ethers include those

-25-

compounds formed from 1,3-butanediol,
1,2,3-trihydroxybutane, 2,3,4-trihydroxy butyric
acid, the aldo- and ketotetroses such as erythrose
and erythrulose, respectively, the aldo- and
5 ketopentoses such as ribose and xyloketose,
respectively, the aldo- and keto-hexoses such as
glucose and fructose, respectively, as well as from a
saccharide such as sucrose or maltose. (It is to be
understood that although diallyl ethers are referred
10 to as reaction products of allyl alcohol and a
polyhydric alcohol, those ethers are most frequently
prepared by a Williamson-type synthesis from an allyl
halide and a strongly alkaline aqueous solution of
polyhydric alcohol. It is to be further understood
15 that mixtures of positional isomers are often
obtained by such reactions. Additionally, mixtures
are obtained that contain more or less than one mole
of allyl group per molecule ether, but contain an
average of about two moles of allyl groups per
20 molecule of ether.) Particularly preferred second
cross-linkers are diallyl tartardiamide (DATDA) and a
diallyl PEG ether that contains an average of one to
three PEG repeating units per molecule.

A further useful second cross-linker is
25 triallylamine. It is well known that diallyl
group-containing compounds wherein the allyl groups
are separated by three atoms such as in diallylamine
and diallyl ether form cyclic compounds when
polymerized. As a consequence, such compounds do not
30 contribute well to cross-linking, but rather tend to
co- or homopolymerize. A particular example of this
phenomenon is diallylamine, which when protonated
during polymerization as would be the case here,
forms six- and/or seven-membered ring, straight chain
35 homopolymers. Triallylamine is useful herein because

-26-

it can form cross-links in addition to cyclizing. It is noted that the minimum chain length of the before-mentioned bis- or di-allyl second cross-linkers is at least three atoms as to avoid the cyclopolymerization route.

The mixed first and second water-soluble, copolymerizable cross-linking agents are present in the monomeric mixture and polymerized hydrocolloid in an amount of about 0.005 to about 0.10 mole percent, and more preferably at about 0.01 to about 0.07 mole percent, based upon the total moles of copolymerizable monomer present in the monomer mixture. When utilized at a concentration below the above minimum, the percentage of extractables becomes too great. When utilized at a concentration above the above maximum, absorbancy values become too low.

As noted earlier, the two cross-linkers are preferably present at a mole ratio to each other of about 1:1.5 to about 1:15, more preferably at about 1:4 to about 1:10, and most preferably at a ratio of about 1:5 to about 1:7, of first cross-linker to second cross-linker. The reason for those mole ratios stems from the absorbancy and percentage extractables performance data obtained. The underlying chemical, mechanistic, basis for the observed result is unknown, but may have to do with the different reactivities of the cross-linkers.

The reason for utilizing the mixture of two cross-linkers as compared to a single cross-linker as described in the prior art is also related to the observed performance of hydrocolloid polymers prepared using single cross-linkers as compared to the mixture. As will be seen from the specific examples that follow, when the dual cross-linker mixture is used, several unexpectedly improved

-27-

hydrocolloid properties are observed as compared to the use of a single cross-linker.

Those improved properties are an increase in absorbancy in deionized water or one percent sodium chloride (saline) solution for a given level of extractables, or conversely, a decreased level of extractables for a given amount of absorbancy in either fluid. In addition, the level of residual monomer that remains after polymerization is completed is reduced when a dual cross-linker mixture is used as compared to use of either the first or second cross-linker alone.

A hydrocolloid polymer of the present invention, when partially neutralized with potassium or sodium hydroxide to an extent of about 60 mole percent of the acid groups present, sorbs about 600 to about 1200 milliliters of deionized or distilled water per dry gram (ml/g) of polymer using the procedures described hereinafter. More preferably, about 800 to about 1200 ml/g are sorbed, and most preferably, about 1000 to about 1200 ml/g are sorbed.

A hydrocolloid polymer of the present invention partially neutralized as described above also sorbs about 50 to about 140 g/ml of a one percent sodium chloride solution using the procedures described hereinafter. More preferably, that saline sorption amount is about 50 to about 110 ml/g.

Another feature of a hydrocolloid polymer of the present invention is the amount of extractables that are obtained from a polymer neutralized as described above using a procedure described hereinafter that utilizes distilled or deionized water in an extraction procedure. The percentage of extractables, based upon the initial dried weight of

-28-

polymer, is less than about 45 percent and can be as low as about 25 percent. Preferred amounts of extractables are about 30 to about 40 weight percent.

5 Yet another unusual feature of a hydrocolloid polymer of the present invention is the relatively low level of unreacted monomer that remains in the polymer after the polymerization reaction has been completed. A hydrocolloid polymer
10 of the present invention contains about 250 to about 1000 parts per million (ppm), and more preferably about 250 to about 500 ppm, residual unreacted monomer per weight of dried polymer after polymerization has been completed.

15 It is to be emphasized that the improved properties of a hydrocolloid polymer of the present invention discussed above, particularly those of distilled or deionized water sorption and extractables, are properties that are exhibited
20 together in a given polymer. Thus, using a single cross-linker, an amount of deionized or distilled water sorption such as those described above can be obtained, but not with the relatively low amount of extractables described. Similarly, a hydrocolloid
25 polymer exhibiting the relatively low level of extractables can be obtained using a single cross-linker, or even without an externally supplied cross-linker where electron beam polymerization is used for both polymerization and cross-linking, but
30 such a polymer does not exhibit the deionized or distilled water sorbancy discussed.

 Similar results are found with levels of residual monomer. Thus, a relatively low level of residual monomer such as a previously-described level
35 can be obtained by use of a single cross-linker or

-29-

extensive electron beam irradiation. However, the resulting hydrocolloid polymer that exhibits such a property does not also exhibit the before-described sorbancy or percentage extractables levels.

5 While not wishing to be bound by theory, it is believed that the improved hydrocolloid polymer properties observed herein are a result of the differing reactivities of the two types of cross-linker. It is to be remembered that the
10 monocarboxy monomer that comprises at least about 80 mole percent of the polymerizable monomers contains acrylic-type unsaturation; i.e., those monomers are alpha,beta-monoethylenically unsaturated. The majority of the other monoethylenically unsaturated
15 copolymerizable monomers also contain similar unsaturation. The first cross-linker also has acrylic unsaturation, whereas the second cross-linker has allylic unsaturation.

 Examination of the polymerization literature
20 indicates that monomers with acrylic-type unsaturation tend to react well together and tend to form random copolymers. Put more precisely, the reactivity ratios for monomers with acrylic-type unsaturation tend to be similar and greater than
25 zero. Generally, reported reactivity ratios lie between about 0.2 and about 6 for the reaction of a given acrylic-type monomer with itself and with another acrylic-type monomer.

 On the other hand, allylically unsaturated
30 monomers generally do not react well with themselves, and tend to react far better with a co-monomer, such as an acrylic-type monomer. Put more precisely again, allylically unsaturated monomers generally exhibit a reactivity ratio of about zero with
35 themselves and of about 2-30 with another monomer such as an acrylic-type monomer.

-30-

In addition to the relative differences in reactivities with other monomers, acrylic-type monomers are generally more readily polymerized than are allylic type monomers. That is, the rate of polymerization of an acrylic-type monomers is generally faster than is the rate of reaction of allylically unsaturated monomers. That rate difference is generally observed regardless of any other co-monomer that may be present, and is thought to be due to the activation provided to the double bond of the acrylic-type monomer by the adjacent polarizing carbonyl group.

When put into the context of the present invention, it is believed that the first cross-linker molecules tend to polymerize relatively randomly and quickly with the other acrylic-type monomers of the polymerizing monomer mixture. The result of that relatively random and fast polymerization is that a growing polymer chain is formed that contains a relatively random and high cross-link density; i.e. a relatively low molecular weight between cross-links. That relatively random and fast reaction of the first cross-linker with the acrylic-type monomers continues until the concentration of first cross-linker decreases sufficiently to slow the reaction by the laws of mass action, although the random positioning of the formed cross-links should remain.

Most of the cross-linking reaction of the second cross-linker is thought to occur subsequent to much of the reaction of the first cross-linker being over. Due to the relative non-reactivity of the allylically unsaturated monomer with itself, substantially no adjacent cross-links can be formed with the second cross-linker. The relatively slower reaction of the second cross-linker tends to place

-31-

those cross-links nearer the termini of already cross-linked polymers and within newly formed polymer molecules that are formed from monocarboxy and other monoethylenically unsaturated molecules that did not react with polymer containing the first cross-linker.

The resulting polymeric hydrocolloid can therefore be characterized as a mixture of polymeric species some of which are formed relatively early in the polymerization and contain mostly the first cross-linker, some of which are formed relatively late in the polymerization and contain mostly the second cross-linker, and some of which contain a core of relatively closely spaced cross-links formed from the first cross-linker, and termini that contain relatively farther-spaced cross-links formed from the second cross-linker. This hypothetical construct can be used to rationalize the results obtained.

Thus, the early-formed hydrocolloid would be present whether two different cross-linkers are present or not since its presence is probably due to chain termination reactions that are independent of the cross-linker. The hydrocolloid containing both cross-linkers is thought to contain relatively little of the second cross-linker due to its low rate of reaction. The hydrocolloid that contains mostly second cross-linker contains a relatively widely spaced and small amount of cross-links due its relatively slow rate of reaction.

That predominantly second cross-linker-containing hydrocolloid nevertheless is thought to account for the lowered amount of extractables and relatively low residual monomer content of the resultant hydrocolloid. In addition, the amount of cross-linking added by the second cross-linker to

-32-

hydrocolloid polymers containing both types of cross-linker is not thought to impair the absorbancy of that polymer species.

One can make the following comparison
5 between the before-described hydrocolloid with a similar polymer prepared with an equal molar amount of either component of the mixture. Where only an acrylic-type cross-linker is used, such a monomer can be substantially used up relatively early in the
10 polymerization reaction to provide a hydrocolloid with adequate absorbancy, but a relatively large amount of extractables and residual monomer. Where only an allylic-type cross-linker is used, enough cross-links are formed to provide adequate
15 absorbancy, but here the relatively slow reaction rate and general inefficiency of the reaction contribute to the relatively high amounts of extractables and residual monomers that are observed.

It is to be reiterated that the
20 before-described reasoning and hypothetical constructs are based upon theories and assumptions for which sufficient data for unequivocal proof are not in hand. Nevertheless, the above description provides a rationale for the phenomena observed and
25 for useful extrapolation of the data that are in hand.

The polymerization reaction utilized to form a hydrocolloid of the invention can be by any known means by which such polymerization reactions can be
30 ordinarily carried out.

Exemplary means of polymerization include the particularly preferred electron beam method described in detail hereinafter as well as other radiative processes such as by the use of gamma
35 radiation and actinic light, preferably in the

-33-

presence of a photosensitizer. Additional means include use of a free radical initiator and heat such as azobisisobutyronitrile, or sodium or potassium thiosulfate, peroxide initiators such as t-butyl
5 hydoperoxide or benzoyl peroxide; and oxidation-reduction (redox) polymerization utilizing a redox couple such as hydrogen peroxide and ascorbic acid. The polymerizations can be carried out in water, as is preferred, or an appropriate mixed
10 solvent such as a water-methanol mixture. The polymerization reaction can also be carried out using so-called inverse phase polymerization techniques that utilize an organic solvent such as hexane as the continuous phase, an appropriate water-in-oil
15 surfactant and an aqueous solution of all of the monomers.

More specifically, the utilization of a free radical-initiating catalyst in an aqueous solution to effectuate polymerization of monomers is described in
20 U.S. Patent No. 3,686,024 to Nankee et al. Photoinduced polymerization processes are described in U.S. Patents No. 4,167,464 to George; No. 4,178,221 to Boutin et al. and No. 4,308,148 to Boutin et al. The use of ionizing radiation to
25 effect polymerization is described in U.S. Patents No. 3,764,502 to Restaino; No. 4,192,727 to Ward; and No. 4,411,754 to Kaetsu et al. The use of electron beam ionizing radiation to effect polymerization as described in U.S. Patent No. 4,192,727 is
30 particularly preferred herein. The disclosures of the above-listed patents are herein incorporated by reference.

A hydrocolloid polymer of the present invention is typically prepared from an aqueous
35 solution of the monomers and cross-linkers, described

-34-

previously. That aqueous solution typically contains about 55 to about 70 weight percent solids (monomers and cross-linkers), and more preferably about 60 to about 65 weight percent solids.

5 A hydrocolloid polymer of the invention is typically utilized as a sorbent in an article of manufacture such as a sanitary napkin, a surgical or wound dressing, a diaper, a wipe or the like. In such an article of manufacture, the hydrocolloid
10 polymer is contained in and on a supporting fibrous web matrix and constitutes a portion of what is commonly referred to as an absorbent layer (or sorbent layer since both absorption and adsorption can occur) because most such products contain a
15 plurality of layers that each serve a particular function.

The hydrocolloid polymer is often utilized in a sorbing article in the form of a powder that is typically prepared by drying and then pulverizing the
20 polymerized material, or the hydrocolloid polymer is prepared in situ on a supporting web that is thereafter dried as a unit. The sorbent layer comprising a supporting fibrous web matrix and hydrocolloid polymer, however applied, can be
25 referred to as a "polymer-containing web", a "hydrocolloid-containing web" or a "polymer-coated web".

More specifically, the hydrocolloid polymer is distributed within a water-insoluble fibrous
30 matrix web that comprises a substantially high loft, resilient fibrous web layer, and is present in an amount of about 200 to about 1500 percent by weight add-on to the matrix based upon the weight of fibrous matrix. Most preferably, the hydrocolloid polymer is
35 present at about 500 to about 1000 percent weight

-35-

add-on. Thus, the matrix plus hydrocolloid polymer constitute a hydrocolloid polymer-containing web or sorbing layer.

5 Frequently, one or more additional webs are placed adjacent to or disposed on one or both surfaces defined by the hydrocolloid polymer-containing web to form a sorbent laminate. Such additional webs can constitute a so-called "wicking layer" that functions to transport the
10 liquid to be sorbed to the hydrocolloid polymer. An additional web can also constitute a water-impermeable membrane that provides an outside surface to the article such as a diaper, or a water-permeable layer that constitutes an inner layer
15 of the article.

Where a powdered form of the hydrocolloid polymer is utilized, it can be sprinkled onto and into the interstices of a fibrous web matrix, and thereby form a coating on the web matrix. It is
20 often desirable to slightly moisten either the web or hydrocolloid polymer powder prior to causing contact therebetween so that the fibers of the web adhere to the powdered polymer as well as physically entrapping the powder.

25 More preferably, the hydrocolloid is prepared in situ on the resilient fibers of the fibrous web matrix. Here, the web is sprayed or submerged or otherwise coated with an aqueous solution of the appropriate, partially neutralized
30 monomer and cross-linkers, and the polymer thereafter formed. Preferably, the polymer is formed by use of irradiation such as electron beam irradiation.

The hydrocolloid polymer coating is present arrayed around, between and on the resilient fibers
35 of the fibrous web matrix of the sorbing layer in an

-36-

intermittently dispersed form. The hydrocolloid polymer is in the form of particles that can be in the shape of fibers, spheres, bits of film when added as a pre-formed dry powder. When polymerized
5 in situ, the hydrocolloid polymer provides globules and bits of film-like particles that are adhered to and around the fibers of the fibrous web. As a consequence, a polymer-containing web made by in situ polymerization can be distinguished from a similar
10 web made by adding the pre-formed dry powder.

Sorbent layers comprising a web matrix coated with hydrocolloid polymer are most preferably prepared by electron beam irradiation. Here, in a laboratory preparation, a web matrix is submerged in
15 an aqueous solution of monomers and cross-linkers as described before, placed into a polyethylene bag so that the plane of the web is parallel to the major plane defined by the sides of the bag, and the bag is sealed. The bag and its contents are then
20 irradiated. The bag is thereafter turned over and irradiated again. Powder samples are similarly prepared except that the bags are free of the matrix, and are not turned over.

The amount of irradiation used to polymerize
25 the monomers and cross-linkers is expressed in megarads (Mrads) per side of the irradiated bag and sorbent layer. Thus, the expression 2-2 is used herein to indicate that each side of the bag and sorbent layer therein was irradiated with 2 Mrads.
30 Similarly, the expression 2-2, 4-4 indicates that a single irradiation of 2 Mrads was used for each side, and was followed by single irradiations of 4 Mrads on each side. Powder sample hydrocolloid polymers prepared by such irradiation are expressed as one or
35 more single numbers as compared to paired numbers to indicate the dose.

-37-

Add on of hydrocolloid to a fibrous web matrix to form a sorbent layer is determined by weighing a known area of dried sorbent layer subtracting the weight of a similar area of starting web matrix and dividing the resulting number by the weight of that area of starting web matrix. Add on is thus expressed as a ratio of the hydrocolloid polymer weight relative to the weight of the starting web matrix.

It is of some import to the function of the sorbing layer formed by the resilient fibrous web matrix and hydrocolloid polymer to have that polymer present in a quantity that is sufficient to sorb a desired amount of liquid, and spaced on and within the web in a manner such that gel blocking does not substantially occur. Gel blocking occurs when hydrocolloid polymer is present in a sufficient quantity and spaced so closely together that as the particles imbibe liquid and swell, a layer of gel is formed that blocks further penetration of liquid into the layer. The in situ polymerization technique described herein, when used to provide about 200 to about 1500 percent add-on of hydrocolloid polymer, provides a sufficient amount of liquid sorbency while exhibiting a relatively minimal amount of gel blocking, if any.

In particularly preferred practice, a sorbent laminate comprised of the supporting fibrous web matrix that contains the hydrocolloid polymer (sorbing layer), and one or more adjacent webs such as wicking layers are compressed as a composite after polymerization and before drying, with the fibrous web layer being maintained in the compressed state by the dried hydrocolloid polymer. The sorbent laminate is compressed to substantially reduce its thickness.

-38-

For example, such a structure is compressed sufficiently to reduce the thickness of the laminate structure by at least 50 percent and the pressure utilized in conjunction with drying is sufficient to
5 cause the composite to remain compact after the pressure is released. The compression utilized should not be so high as to substantially crimp or crease the resilient fibers of the fibrous layer. Upon wetting the fibrous matrix, the hydrocolloid
10 becomes wet so that the fibrous layer expands from its compressed state due to the inherent resilience of the fibers of that layer, and thereby facilitates swelling of the hydrocolloid polymer.

Where a hydrocolloid-containing compressed
15 sorbent web is utilized for a sorbent article, the starting fibrous web matrix (prior to the addition of hydrocolloid polymer) has an initial dry bulk recovery of at least about 30 percent, and more preferably at least about 60 percent, an initial dry
20 bulk of at least about 20 cubic centimeters per gram (cc/g), and a weight of less than about 2 oz/yd - (about 68 gm/m²).

The initial dry bulk is the area times thickness of the layer under the load of 0.01 pounds
25 per square inch calculated in cubic centimeters. This value is divided by the weight in grams to provide the measurement in cubic centimeters per gram.

The dry bulk recovery is obtained by
30 subjecting the web to a load of 1.75 pounds per square inch (psi) for five minutes, removing the load and allowing the web to rest for one minute, subjecting the web to a load of 0.01 psi for one minute and then measuring the final dry bulk under
35 the 0.01 psi load. The dry bulk recovery is the final bulk divided by the initial bulk expressed in percent.

-39-

If the fibrous web can provide this dry bulk recovery and has an initial dry bulk of at least 20 cc/gm with a web weight of less than 2 oz/yd², the fibrous web meets the requirements of the sorbing layer. When the fibrous web matrix has these requirements, it can retain hydrocolloid polymer up to at least 1,500 percent of the dry basis weight of the web. It is preferable that the web contain 200 percent to 1,500 percent by weight dry basis hydrocolloid, relative to the dry basis weight of the web.

A suitable fibrous web for a sorbing layer has a substantially high loft, and has a tendency to return substantially to its original thickness on compression followed by release. The resulting resiliency of the fibrous web typically permits a sorbing layer containing a hydrocolloid polymer to regain at least about 75 percent of its original thickness when it is released from its compressed state as liquid penetrates the sorbent product.

Such webs are typically formed from synthetic staple fibers such as polyethylene, polypropylene, polyester, nylon, bicomponent fibers and the like are particularly desirable. Cellulosic fibers such as rayon can also be used.

The fibrous web can be formed by carding, dry laying or wet laying fibers so as to provide a low density structure, as is well known in the art. In one preferred embodiment, staple polyester fibers are air laid with a minor portion of fusible fibers to form a web whose fibers are lightly bonded by passing hot air through the web fibers making the fusible fibers tacky so as to stick to each other and the staple fibers to provide further integrity to the web structure.

-40-

The wicking layer is comprised of substantially uniformly disposed, frictionally engaged particles of hydrophilic fibers, such as rayon fibers, cellulosic fibers, or peat moss, or mixtures thereof. The cellulosic fibers include wood pulp fibers, cotton linters, and the like. The wood pulp fibers generally are those that are used to form the fluff or fibrous batt layer in conventional sorbent products such as disposable diapers, sanitary napkins, etc. Other cellulosic fibers that can also be used are rayon fibers, flax, hemp, jute, ramie, cotton and the like. The particles of fibers or peat moss or mixtures thereof are placed in such a way as to form a layer in which the particles are spaced sufficiently close to one another so as to promote rapid movement of liquid (wicking) in the plane of the layer. Typically, there is a transition zone between the sorbent web and wicking layer that comprises portions of the engaged wicking layer particles that extend into the hydrocolloid polymer and become integral therewith so that those particles are in intimate contact with the hydrocolloid polymer.

An exemplary compressed, composite useful in a diaper can be prepared as follows.

The sorbent composite is made by four steps. First, a fibrous web structure is made by blending polyester fiber T-375W manufactured by DuPont and fusible BICO 1040 fiber, made by BASF, in a ratio of 67/33 percent by weight. This blend is carded into a high bulk non-woven web structure of approximately 1.20 oz/yd² (about 40.7 g/m²) weight and passed through an air bonder at a temperature of 325° F (about 163°C) for a duration of 5.6 seconds and at a pressure differential of 0.25

-41-

inches (0.64 cm) of water. This heat process bonds the web by partially melting the BICO fiber.

The second step consists of applying to that web a coating of potassium acrylate solution at a concentration of about 65 percent solids and about 60 percent neutralized monocarboxy monomer containing a total of 0.05 mole percent of methylene bisacrylamide and diallyl tartaramide at a 1:5 mole ratio. The monomer is added by suction coating to a desired level of 12.0 oz/yd² (about 40 g/m²) of dry coating weight. The thus applied coating is polymerized and cross-linked into a hydrocolloid polymer by multiple electron beam irradiations of 2 Mrads and 2 Mrads with an ESI 300 KV electron accelerator.

Pulp wicking layers are attached as the third step. Prior to this, the polymer is adjusted to a 25 percent moisture content. It is passed through the suction zone of a Hammermill where pulp is defiberized and deposited at a weight of 4.8 oz/yd² (about 162.75 g/m²). The use of vacuum causes at least some of the deposited fibers to migrate into the polymer-containing web and become integral therewith. Pulp is applied to the other side similarly. In other embodiments, pulp layers of about 50 g/m² are used. The entire composite is lightly sprayed with water to provide a moisture content of the pulp of about 10 percent by weight. The resulting web is thereafter compressed to a thickness of 0.143 inches (about 0.36 cm), and then dried for use. A useful sorbent layer can also be prepared in compressed form having a single wicking layer or no wicking layer.

Upon release of pressure, the pulp has formed into a high density layer with a capillary

-42-

size suitable for liquid wicking and the resilient fiber layer remains compressed. Upon use of the resulting dry structure, when a significant amount of liquid contacts the surface and migration of liquid into the sorbent layer takes place, the hydrocolloid polymer becomes soft and releases the resilient fibers so that the thickness of the structure increases markedly. This increase in thickness provides an area for storage of liquid.

Further details concerning compressed composite sorbing products as discussed above, and their sorbing layers can be found in U.S. Patents No. 4,500,315; No. 4,537,590; No. 4,540,454; and No. 4,573,988, all to Pieniak et al., whose disclosures are incorporated herein by reference.

It is noted that when a hydrocolloid polymer of the invention is employed as a portion of a sorbent layer of a sorbing article and polymerized in situ by an electron beam as described before, the liquid sorbing properties of the polymer are reduced as compared to the same properties of a similar polymer prepared separately. The reason for the difference in properties is thought to reside in the fact that the dose of radiation utilized for an in situ polymerization process is generally greater than that required for formation of a hydrocolloid prepared free in an aqueous medium. The liquid sorption properties of webs so produced are however improved over the same properties obtained utilizing a single cross-linker or obtaining cross-linking solely via the electron beam. It is further noted that that in situ polymerization process provides enhanced (lower) levels of extractables.

A hydrocolloid polymer in situ polymerized on the matrix fibers of a fibrous web typically

-43-

exhibits sorptions of a 1 percent saline solution of about 25 to about 45 g/ml (about 250 to about 450 percent), and more preferably about 30 to about 40 g/ml. Extractables levels of an in situ web-polymerized hydrocolloid polymer are typically between about 10 to about 20 percent.

Best Mode For Carrying Out The Invention

A. Testing Procedures

Several testing procedures have been utilized to analyze the hydrocolloid polymers of the present invention and to compare them with other hydrocolloid polymers. Details of those testing procedures are described hereinbelow.

1. Residual Monomer

Residual monomer levels are determined by high-performance liquid chromatography (HPLC). The monomers assayed are acrylic acid and its ester dimer. Glacial acrylic acid, in an amount of about 500 milligrams (mg) is weighed to the nearest 0.1 mg into a 100 milliliter (ml) volumetric flask and is diluted to volume with 0.01 N sulfuric acid to form Solution A. Acrylic acid ester dimer (at least 95 percent pure) in an amount of about 100 mg is weighed to the nearest 0.1 mg into a second 100 ml flask, and is diluted to volume with 0.01 N sulfuric acid to form Solution B. Each of Solutions A and B is mixed thoroughly.

Solution A (10 ml) and Solution B (10 ml) are pipetted into a third 100 ml volumetric flask and diluted to volume with 0.01 N sulfuric acid to form Working Standard I (WS I). Working Standard II (WS II) is prepared similarly using 1 ml of each of Solutions A and B. Each Working Sample solution is mixed thoroughly.

-44-

Duplicates of each WS I and WS II are prepared. Portions of each of the four standards are placed into autosampler vials and capped.

5 A powder sample of hydrocolloid polymer of about 125 mg, weighed to the nearest 0.1 mg, is weighed into 50 ml centrifuge tube. (Powdered hydrocolloid polymers discussed herein are sized to pass through a 20 mesh sieve, U.S. Standard Sieve series.) Twenty-five ml of 0.1 N sulfuric acid are
10 added to the tube and the tube is capped. The capped tube is shaken on a mechanical wrist shaker for 20 minutes. An aliquot is removed, filtered through a 0.45 micron disposable filter, placed into an autosampler vial, and the vial is capped to provide
15 an acid extract sample. A duplicate sample is similarly prepared.

A generally similar procedure is utilized for sorbent layers comprised of a web matrix coated with hydrocolloid polymer except that approximately
20 1.0 gram (g) of the coated web, weighed to the nearest 0.1 mg, is weighed into a 30 ml serum vial. The above amount of sulfuric acid is added and the vial is capped and sealed. Where sorbency is too great to permit ready extraction, 30 ml of 0.1 N
25 sulfuric acid are used with a larger serum vial.

A Waters Associates HPLC equipped with a model M-590 pump, a model M-481 ultraviolet detector (set at 214 nm) and an autosampler is used. The HPLC uses an Aminex[®] HPX-87H ion exchange (Bio-Rad)
30 column and a guard column. Sulfuric acid (0.01 N) is used as the mobile phase.

In a typical analytical assay, instrumental settings are:

-45-

Flow rate: 0.80 ml/minute
Injection volume: 20 microliters (ul)
Wavelength: 214 nm
Column heater 40°C
5 temperature:
Range: 0.05 AUFS

Retention times typically found are:

10 Acrylic acid 14.6 minutes
Ester dimer 17.7 minutes

15 The HPLC is run for about 30 minutes prior to use or until a stable baseline is obtained. Samples of WS I and WS II are injected. Duplicate samples of WS I and WS II are injected and the areas/mg of both runs for each sample determined. The values of area/mg should agree within ± 2 percent of their averages or the runs are repeated. Response factors for each sample are also calculated.

20 An aliquot of each sample extract to be assayed is injected once. The results for each pair of duplicate samples should agree within ± 3 percent or the duplicate samples are reassayed.

25 The amounts of acrylic acid and its ester dimer present in the sample are thereafter calculated from the areas of the HPLC chart, the response factor, the dilution factor and sample weight using a standard equation, and are expressed in parts per million of the original sample.

30

2. Percentage Extractables

Percentage extractables are determined in a manner generally similar to the manner of determining residual monomer. In this case, however, a standard of polyacrylic acid (PAA) of a molecular weight of about 80,000 is utilized.

35

-46-

More specifically, approximately 200 mg of PAA, weighed to the nearest 0.1 mg, are weighed into a 100 ml volumetric flask and diluted to volume with 0.2 molar (M) Na_2SO_4 as mobile phase. Glacial acrylic acid (GAA; 500 mg) weighed as before into a 500 ml volumetric flask and diluted to volume with the mobile phase serves as a GAA standard solution. Aliquots (10 ml and 1 ml) of the GAA standard solution are each diluted with mobile phase to 100 ml in separate 100 ml volumetric flasks serve as working standards.

The powder sample of hydrocolloid polymer (150 mg) weighed as before is placed into a 50 ml centrifuge tube to which 25 ml of 0.2 M Na_2SO_4 are added. The tube is capped and shaken on a mechanical wrist shaker for 25 minutes, filtered as before into an autosampler vial, and the vial is capped. If the filtrate is not clear, the cloudy filtrate is returned to the centrifuge tube, the tube is centrifuged and the supernatant filtered as above. The sorbent layer samples are prepared as discussed previously, and assayed as discussed above. The standards and samples are prepared as in duplicate.

The HPLC is run as described before.
Typical instrument settings are:

Flow rate:	10 ml/minute
Injection volume:	20 ul
Wavelength:	214 nm
Column heater	
temperature:	40°C
Range:	0.2 AUFS

35

-47-

Retention times typically found are:

PAA	6.7 minutes
Acrylic acid	9.9

5 A size exclusion stationary phase (3000 PW) is used with a Toyo Soda TSK guard column.

 The working standards of PAA and GAA are injected separately and their retention times are determined. Duplicates of each standard are run.
10 The areas/mg for each of the two injections should agree within ± 5 percent of their average for each standard, or the standardization procedure is repeated. The response factors are calculated for the standards.

15 Each sample to be assayed is injected once. The results for each pair of duplicate samples should agree within ± 5 percent of their average, or the samples are run again.

 Both high and low molecular weight polymers
20 are extractable. The high molecular weight percentage extractables is related to the 80,000 molecular weight standard using the response factor for that polymer, whereas the low molecular weight percentage extractables is related to the monomer
25 standard using the response factor for the monomer.

 The percentage extractables for high and low molecular weight polymers are calculated separately, each using the appropriate peak areas and response factors, as well as the dilution factor, and sample
30 weight. The individual extractables percentages are then summed to provide the extractables percentage.

3. Fluid Sorption

 Fluid sorption by a hydrocolloid polymer is
35 determined as follows. A powder sample is dried in a

-48-

vacuum oven for about 18 hours at a temperature of 40° C. An aliquot of about 100 mg, weighed to the nearest 0.1 mg, is added to 200 ml of deionized water, and permitted to sorb the water for a time
5 period of 2 hours.

A filter paper is soaked with deionized water and allowed to drain until no further drops of water appear. The wet filter is thereafter weighed.

The mixture of hydrocolloid polymer and
10 water is thereafter filtered through the wet filter paper. After no further drops of water are apparent, the combined wet filter paper and swollen hydrocolloid are weighed to provide a total weight. Subtraction of the weight of dried hydrocolloid
15 polymer powder and wet filter paper from the total weight provides the weight of sorbed deionized water, which is expressed as a percentage of the original weight of the dried hydrocolloid polymer weight, or in milliliters of deionized water sorbed per gram of
20 dry hydrocolloid polymer.

A similar procedure is utilized for sorbent layers comprised of a web matrix coated with a hydrocolloid polymer. In both cases, the study is carried out at ambient room temperature, without
25 stirring. Sorption studies of 1 percent sodium chloride (saline) solutions are carried out similarly except that 1 percent sodium chloride in deionized water is used in place of the deionized water.

30 B. Hydrocolloid Polymers

1. Single Cross-linker Preparations

A series of hydrocolloid polymers was prepared by electron beam irradiation using a single 2 Mrad irradiation in polyethylene bags. Those
35 polymers were prepared from 60 mole percent

-49-

neutralized acrylic acid using various mole percentages of five different, single cross-linkers, and were polymerized at 65 weight percent solids. After drying the resulting polymers and crushing the dried solid, sorbency of deionized water was determined and plotted as a function of the mole percent cross-linker. Those results are shown in Figure 1.

As can be seen from that Figure, a cross-linker with a relatively high reactivity, methylenebisacrylamide (MBA), generally provided lower sorbency than did a cross-linker with a relatively lower reactivity, diallyl tartardiamide (DATDA), when both were used at equimolar concentrations.

Extractables percentages for the polymers cross-linked with MBA and DATDA were determined. Those values were compared to similar partially neutralized acrylic acid polymers that were prepared by irradiation with 2, 4 and 8 Mrad doses provided as multiple 2 Mrad doses with no externally supplied cross-linker to serve as control. Here, sorbency of deionized water was plotted against the extractables percentages, and the results of that plotting are shown in Figure 2.

As can be seen from Figure 2, the percentage extractables and sorbency decreased as mole percentage cross-linker increased (0.01, 0.03 and 0.05) or irradiation dose increased (2, 4 and 8 Mrads). The percentage of extractables decrease was about equivalent to increasing the radiation dosage for the control, in the range of about 600-1000 ml/g swell (sorption).

The data also show that for a desired swell value in deionized water, the extractables percentage

-50-

level remains about constant in the about 600-1000 ml/g range. Deviations occur at lower swell (sorption) capacities that are below those contemplated herein.

5 2. Mixed Cross-linker Preparations

Powdered hydrocolloid polymers of the invention were prepared in plastic bags using a single 2 Mrad dose of irradiation. Two groups of polymers were prepared as described before in which
10 the total cross-linker concentration was either 0.03 or 0.05 mole percent of the partially neutralized acrylic acid monomer, and the mole percentage of MBA and DATDA were varied relative to each other.

Data for sorption of deionized water and 1
15 percent sodium chloride are shown as a function of the mole percentage of MBA in the total amount of cross-linker in Figures 3 and 4, respectively. Data points for two of those hydrocolloid polymers [MBA:DATDA = 0.01:0.04 (●) and = 0.02:0.03 (Δ)] are
20 shown in Figure 5 superimposed on the graph of Figure 2.

The data of Figures 2 through 5 illustrate that relatively higher swells can be produced at relatively lower extractables percentage values by
25 using a combination of cross-linkers as taught herein, as compared to using a single cross-linker or cross-linking with radiation.

Those data also show that at a low irradiation dose, use of single cross-linker provides
30 a trade off for a higher irradiation dose without cross-linker. The data further illustrate that use of mixed cross-linkers as taught herein with a relatively low irradiation dose provides improved sorption (swelling) at a given level of extractables.

35

-51-

3. Mixed Cross-linker Use in Sorbent Layers

Sorbent layers comprised of a fibrous web matrix coated with hydrocolloid polymer were prepared and their sorptions of 1 percent sodium chloride (saline) were plotted against the percentage of extractables. The fibrous web matrix used for the exemplary studies described herein was the previously discussed 2:1 blend of polyester fiber T-375W and fusible BICO 1040 fiber. Those data are shown in Figure 6 that also shows data for control sorbent layers prepared from similar aqueous solutions of partially neutralized acrylic acid that contained no externally supplied cross-linker at weight add-ons of 5.5:1 and 10:1.

The control sorbent layers were irradiated as follows.: 5.5:1 add-on (Control I; squares) = 2-2; 2-4; and 2-8 (from right to left in the graph), and 10:1 add-on (Control II; triangles) = 2-2, 2-2; 2-2, 4-4; and 2-2, 8-8 (from right to left in the graph). The sorbent layers of the invention were each prepared using 2-2 Mrad irradiations and both were at 5.5:1 add-ons. The compositions used to prepare the sorbent layers of the invention contained MBA and DATDA (designated MBA:DATDA) at the following mole ratios based upon the moles of partially neutralized acrylic acid, from right to left in the graph (X):0.005:0.06, 0.01:0.06, and 0.01:0.04 (the two left-hand-most values were repeats). The single value (O) for a MBA:DATDA mixture contained those cross-linkers at a mole ratio of 0.02:0.03.

The data of Figure 6 show that at an add-on level of 5.5:1, significant improvement in sorption of 1 percent saline is obtained without increasing extractables percentages. Those data also illustrate

-52-

the before-discussed preference for a mole ratio of first cross-linker (e.g. MBA) to second cross-linker (e.g. DATDA) of at least 1:1.5, and preferably a greater amount of second cross-linker.

5 Three of the four MBA:DATA sorbent layers of Figure 6 (first, third and fourth from left to right as shown in the upper portion of that Figure) were compared (Figure 7) to two of the control sorbent layers of that Figure [control layers prepared by 2-8
10 (left) and 2-4 (right) irradiations were used] as to 1 percent saline sorption and residual monomer levels. As can be seen from Figure 7, relatively high saline sorptions with relatively low levels of residual monomer were obtained for the sorbent layers
15 of the invention as compared to the two control sorbent layers.

 Some of the sorbent layers utilized for the data of Figure 7 were also ground to produce a powder that contained a mixture of the hydrocolloid polymer
20 as well as particulate sorbent layer coated with hydrocolloid polymer. The resulting ground powders were thereafter assayed for their abilities to sorb 1 percent saline solutions. Data from this study are shown in the Table below along with the sorption data
25 for the unground sorbent layers.

30

35

-53-

Table

Comparative One Percent
Saline Sorption Data¹

5

	<u>Irradiation</u> <u>Dose</u> ²	<u>Mole %</u> <u>MBA</u>	<u>Mole %</u> <u>DATDA</u>	<u>Unground</u> <u>Layer</u> ³	<u>Ground</u> <u>Layer</u> ⁴
	2-2	0.01	0.04	31	37
10	2-2	0.01	0.06	33	40
	2-8	None	None	22	22
	2-2, 8-8 *	None	None	19	22

15 ¹Sorption of one percent sodium chloride
in deionized water for sorbent layers containing
polymers prepared from 60 mole percent neutralized
polyacrylic acid containing MBA and DATDA at the
molar ratios shown relative to acrylic acid, or with
no cross-linker. All sorbent layers contained a
20 hydrocolloid polymer coating at a weight ratio of
polymer to web matrix of 5.5:1, unless otherwise
indicated.

²Irradiation doses in Mrads as discussed
before.

25 ³Unground Layer = sorption data for a
dried sorbent layer.

⁴Ground Layer = sorption data for a dried
and then ground sorbent layer.

30 *10:1 Add-on of hydrocolloid polymer to
used matrix.

The data of the above Table again illustrate
the approximately 50 percent increase in sorption of
one percent saline of a web of the present invention
35 as compared to a control layer. Those data also

-54-

illustrate that the ground sorbent layer, which is mostly (about 85 weight percent) hydrocolloid polymer of this invention, is also useful as a particulate sorbing agent as when added as a powder to a fibrous web matrix to form a sorbing layer.

The present invention has been described with respect to preferred embodiments. It will be clear to those skilled in the art that modifications and/or variations of the disclosed subject matter can be made without departing from the scope of the invention set forth herein.

15

20

25

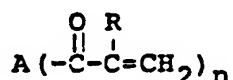
30

35

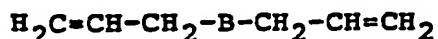
-55-

WHAT IS CLAIMED IS:

1. A water-swellable polymer consisting essentially of about 80 to about 99.995 mole percent polymerized water-soluble alpha,beta-
- 5 monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain, zero to about 19.995 mole percent polymerized water-soluble, copolymerizable monoethylenically unsaturated monomer, and about 0.005 to about 0.10 mole percent
- 10 polymerized water-soluble, copolymerizable cross-linker mixture, said monoethylenically unsaturated monomers containing about 5 to about 70 mole percent free acid and about 30 to about 95 mole percent acid neutralized with a water-soluble
- 15 monovalent cation, said cross-linker mixture consisting essentially of a first and a second cross-linker that are present at a mole ratio to each other of about 1:1.5 to about 1:15 in the order recited, said first cross-linker having a structure
- 20 that corresponds to the formula:



- 25 wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms,
- 30 said second cross-linker having a structure that corresponds to the formula:



35

-56-

wherein B is a divalent radical that is an allylimino radical or contains a chain of 2 to about 10 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms;

5 when partially neutralized with potassium hydroxide in an amount of about 60 mole percent of the polymerized acid groups present, said polymer sorbing about 600 to about 1200 milliliters of deionized water per dry gram of said polymer, and
10 exhibiting less than about 45 weight percent extractables after said sorbing.

2. The water-swellaable polymer of claim 1 containing substantially only said polymerized monocarboxy monomer and said polymerized cross-linker
15 mixture.

3. The water-swellaable polymer of claim 1 wherein said polymerized monocarboxy monomer is a mixture of acrylic acid and an alkali metal or ammonium salt of acrylic acid and said
20 copolymerizable monomer is absent.

4. The water-swellaable polymer of claim 3 wherein said polymerized cross-linkers are present in a mole ratio of about 1:4 to about 1:10 in said recited order.

25 5. The water-swellaable polymer of claim 4 wherein said partially neutralized polymer sorbs about 50 to about 110 milliliters of an one weight percent aqueous sodium chloride solution per dry gram, and exhibits about 30 to about 40 weight
30 percent extractables in deionized water.

6. The water-swellaable polymer of claim 5 wherein said partially neutralized polymer further exhibits about 250 to about 500 parts per million residual monomer.

35

-57-

7. The water-swellaable polymer of claim 5 wherein said first cross-linker is methylene bisacrylamide and said second cross-linker is diallyl tartardiamide.

5 8. A water-swellaable polymer consisting essentially of (a) a polymerized mixture of acrylic acid and an alkali metal or ammonium salt of acrylic acid and (b) about 0.01 to about 0.07 mole percent polymerized cross-linker mixture, said cross-linker
10 mixture consisting essentially of methylenebisacrylamide and diallyl tartardiamide that are present at a mole ratio to each other of about 1:4 to about 1:10 in the order recited, said polymer exhibiting the following properties when about 60
15 mole percent of said polymerized acrylic acid groups are neutralized with potassium or sodium hydroxide:

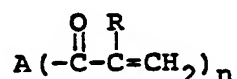
(a) an absorbancy of about 800 to 1200 milliliters of deionized water per dry gram and about 30 to
20 about 40 weight percent extractables;
(b) an absorbancy of about 50 to about 110 milliliters per dry gram in a solution of one weight
25 percent aqueous sodium chloride; and
(c) about 250 to about 500 parts per million residual monomer.

9. A polymer-coated web comprising a water-insoluble fibrous web matrix having coated
30 thereon a water-swellaable polymer, said web matrix having a dry bulk recovery of at least about 30 percent, an initial dry bulk of at least about 20 cc/g and a weight of less than about 2 oz/yd², said water-swellaable polymer being present in an amount of
35 about 200 to about 1500 percent weight add-on to said

-58-

web matrix consisting essentially of about 80 to about 99.995 mole percent polymerized water-soluble alpha, beta-monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain, zero to about 19.995 mole percent polymerized water-soluble, copolymerizable monoethylenically unsaturated monomer, and about 0.005 to about 0.10 mole percent polymerized water-soluble, copolymerizable cross-linker mixture, said monocarboxy monomer being a mixture of about 5 to about 70 mole percent free carboxylic acid and about 30 to about 95 mole percent carboxylic acid neutralized with a water-soluble monovalent cation, said cross-linker mixture consisting essentially of a first and a second cross-linker that are present at a mole ratio to each other of about 1:5 to about 1:15 in the order recited, said first cross-linker having a structure that corresponds to the formula:

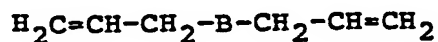
20



wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms,

said second cross-linker having a structure that corresponds to the formula:

30



wherein B is a divalent radical that is an allylimino radical or contains a chain of 2 to about 10 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms;

-59-

when partially neutralized with potassium or sodium hydroxide in an amount of about 60 mole percent of said polymerized acid groups present, said polymer sorbing about 600 to about 1200 milliliters of deionized water per dry gram of said polymer, and exhibiting less than about 45 weight percent extractables after said sorbing.

10. The polymer-coated web of claim 9 wherein said coated web sorbs about 30 to about 45 grams of a one weight percent aqueous sodium chloride solution per dry gram of coated web.

11. The polymer-coated web of claim 9 wherein said polymerized, monocarboxy monomer is a mixture of acrylic acid and an alkali metal or ammonium salt of acrylic acid and said copolymerizable monomer is absent.

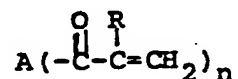
12. The polymer-coated web of claim 9 wherein said polymerized cross-linkers are present in a mole ratio of about 1:4 to about 1:10 in said recited order.

13. A polymer-coated web comprising a water-insoluble fibrous web matrix having coated thereon a water-swellaable polymer, said web matrix having a dry bulk recovery of at least about 60 percent, an initial dry bulk of at least about 20 cc/g and a weight of less than about 2 oz/yd², said water-swellaable polymer being present in an amount of about 400 to about 1200 percent weight add-on of said web matrix consisting essentially of a polymerized water-soluble alpha, beta-monoethylenically unsaturated monocarboxy monomer containing a three carbon atom chain and about 0.01 to about 0.07 mole percent polymerized water-soluble, copolymerizable cross-linker mixture based upon said monocarboxy monomer, said monocarboxy monomer being a mixture of

-60-

about 10 to about 40 mole percent free carboxylic acid and about 90 to about 60 mole percent carboxylic acid neutralized with a water-soluble monovalent cation, said cross-linker mixture consisting essentially of a first and a second cross-linker that are present at a mole ratio to each other of about 1:4 to about 1:10 in the order recited, said first cross-linker having a structure that corresponds to the formula:

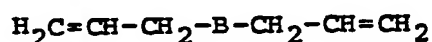
10



wherein R is hydrogen or C₁-C₄ alkyl; n is 2 or 3; and A is a divalent or trivalent radical that contains a chain of 3 to about 30 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms,

said second cross-linker having a structure that corresponds to the formula:

20



wherein B is a divalent radical that is an allylimino radical or contains a chain of 2 to about 10 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms;

when partially neutralized with potassium or sodium hydroxide in an amount of about 60 mole percent of said polymerized acid groups present, said polymer sorbing about 600 to about 1200 milliliters of deionized water per dry gram of said polymer, and exhibiting less than about 45 weight percent extractables after said sorbing.

35

-61-

14. The polymer-coated web of claim 13 wherein said polymerized, monocarboxy monomer is a mixture of acrylic acid and an alkali metal or ammonium salt of acrylic acid.

5 15. The polymer-coated web of claim 13 wherein said polymerized cross-linkers are present in a mole ratio of about 1:5 to about 1:7 in said recited order.

10 16. The polymer-coated web of claim 13 wherein said first cross-linker is methylenebisacrylamide or a PEG diacrylate containing an average of 1 to 9 PEG units per molecule and said second cross-linker is diallyl tartaramide or a diallyl PEG ether containing an average of 1 to 3 PEG
15 units per molecules.

17. The polymer-containing web of claim 13 wherein said hydrocolloid coating is present in an amount of about 500 to 1000 weight percent of the weight of said matrix.

20 18. The polymer-containing web of claim 13 wherein said hydrocolloid polymer is polymerized in situ on the fibers of said fibrous matrix.

19. The polymer-containing web of claim 13 further including a wicking layer disposed on one
25 surface defined by said web, said wicking layer comprising substantially uniformly disposed, frictionally engaged particles of hydrophilic fibers, peat moss or a mixture thereof that are placed in such a way as to form a layer in which said particles
30 are spaced sufficiently close to one another so as to promote rapid movement of liquid in the plane of said layer, said polymer-containing web and said wicking layer together constituting a sorbent laminate.

20. The sorbent laminate of claim 19
35 further containing a transition zone between said

-62-

said polymer-containing web and said wicking layer
that comprises portions of said engaged wicking layer
particles that extend into said hydrocolloid polymer
such that said particles become integral with said
5 hydrocolloid polymer and are in intimate contact
therewith.

21. The sorbent laminate of claim 19 in a
form compressed to substantially reduce its thickness.

10

15

20

25

30

35

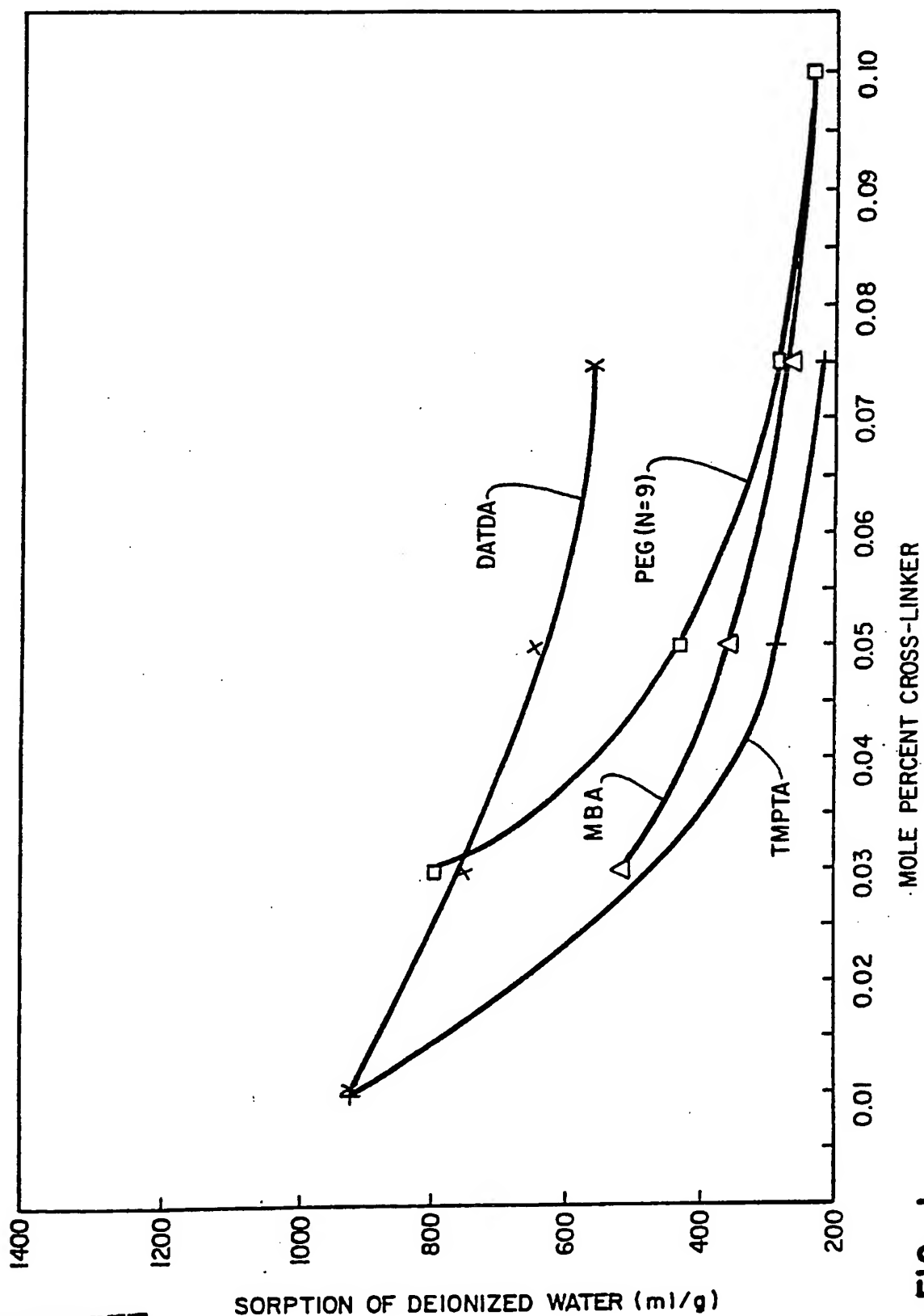


FIG. 1

SORPTION OF DEIONIZED WATER (ml/g)

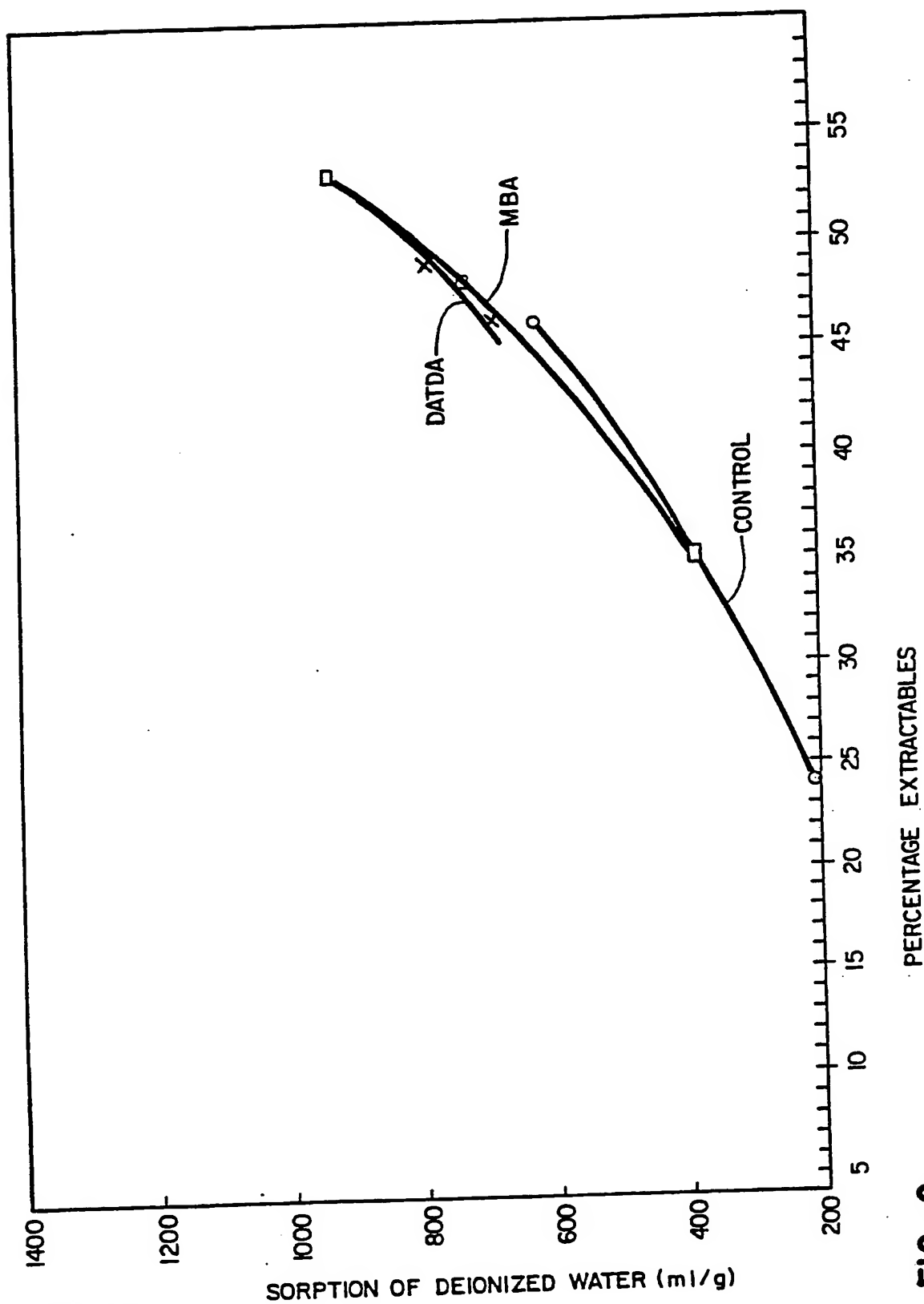


FIG. 2

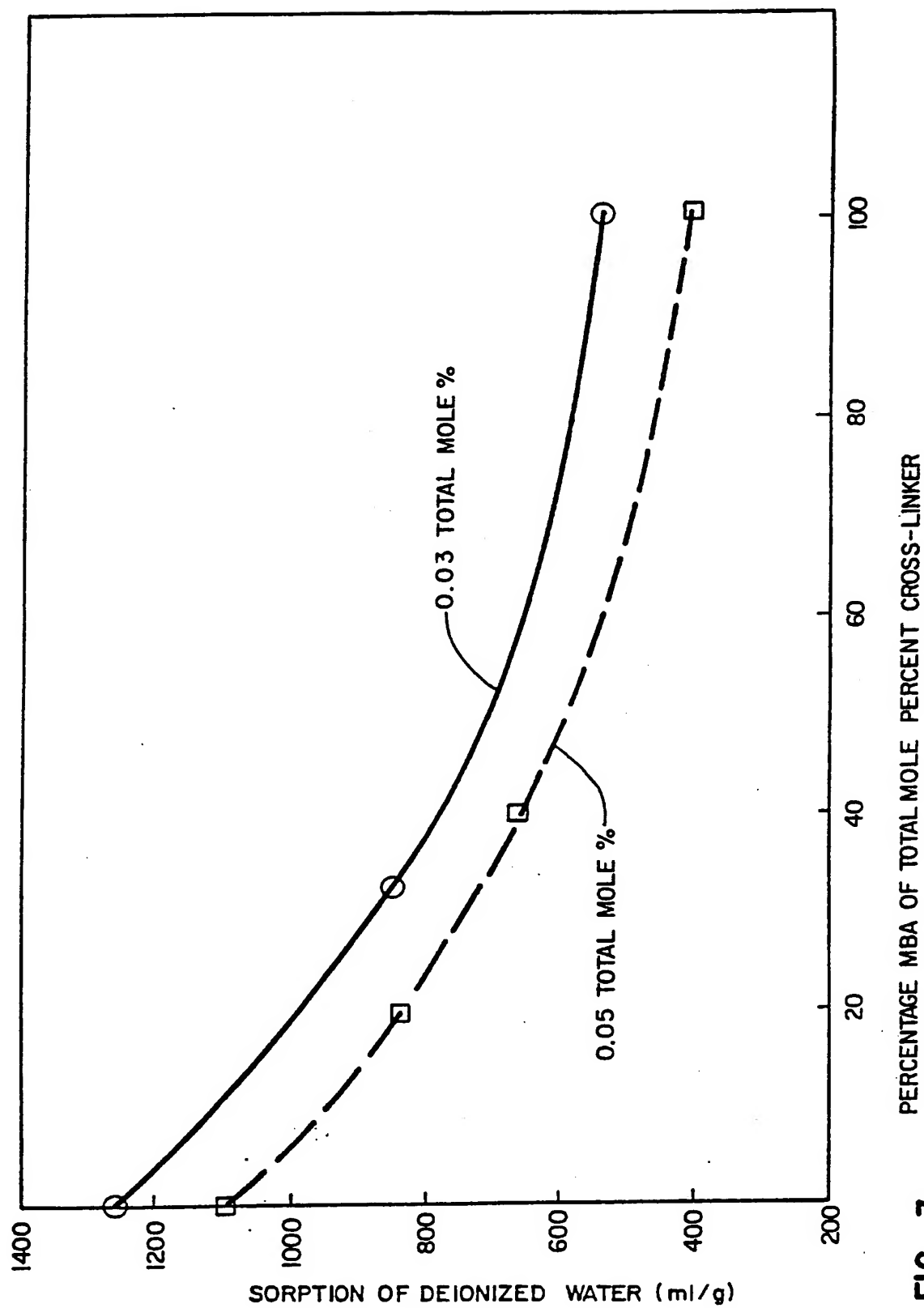


FIG. 3

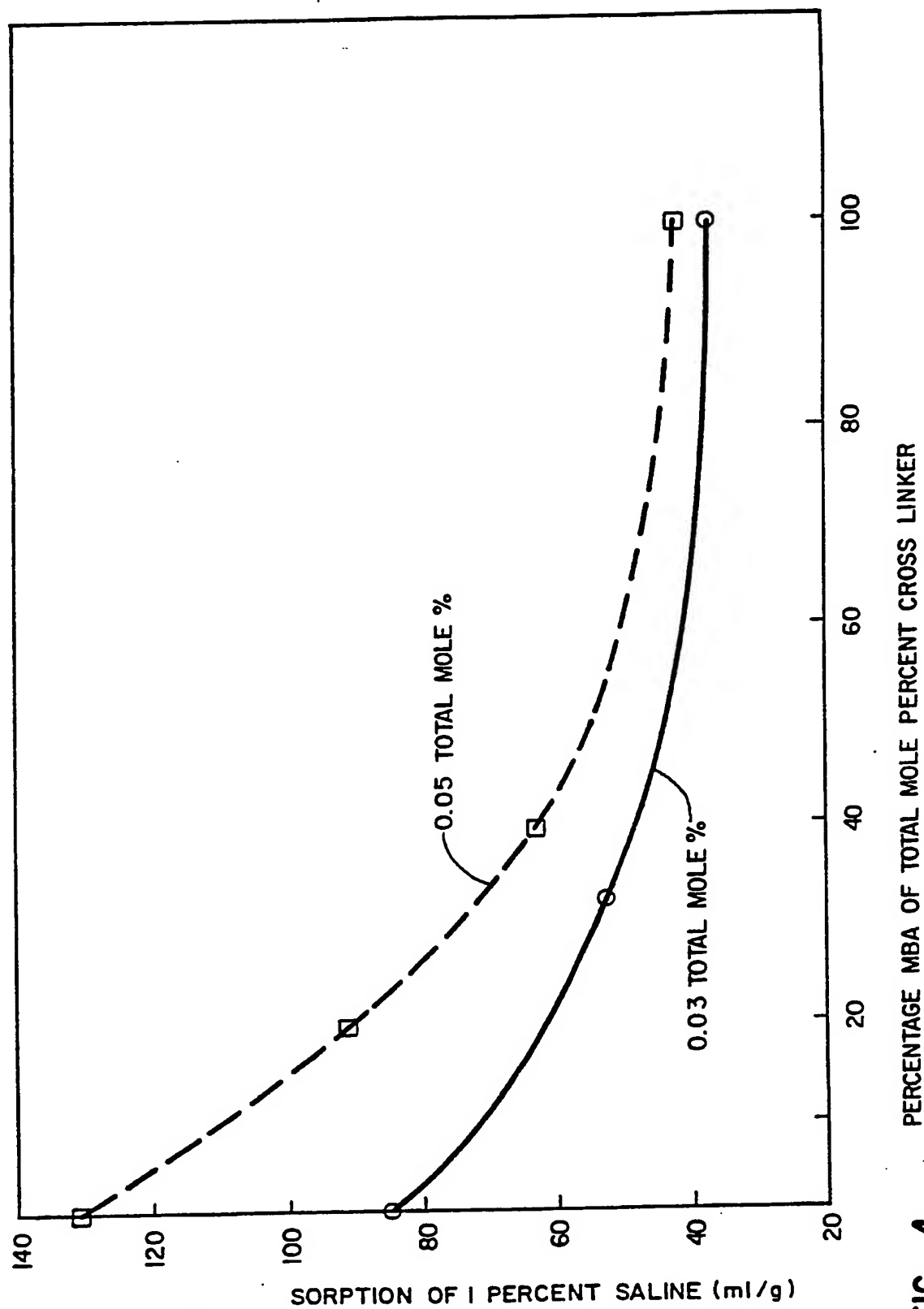
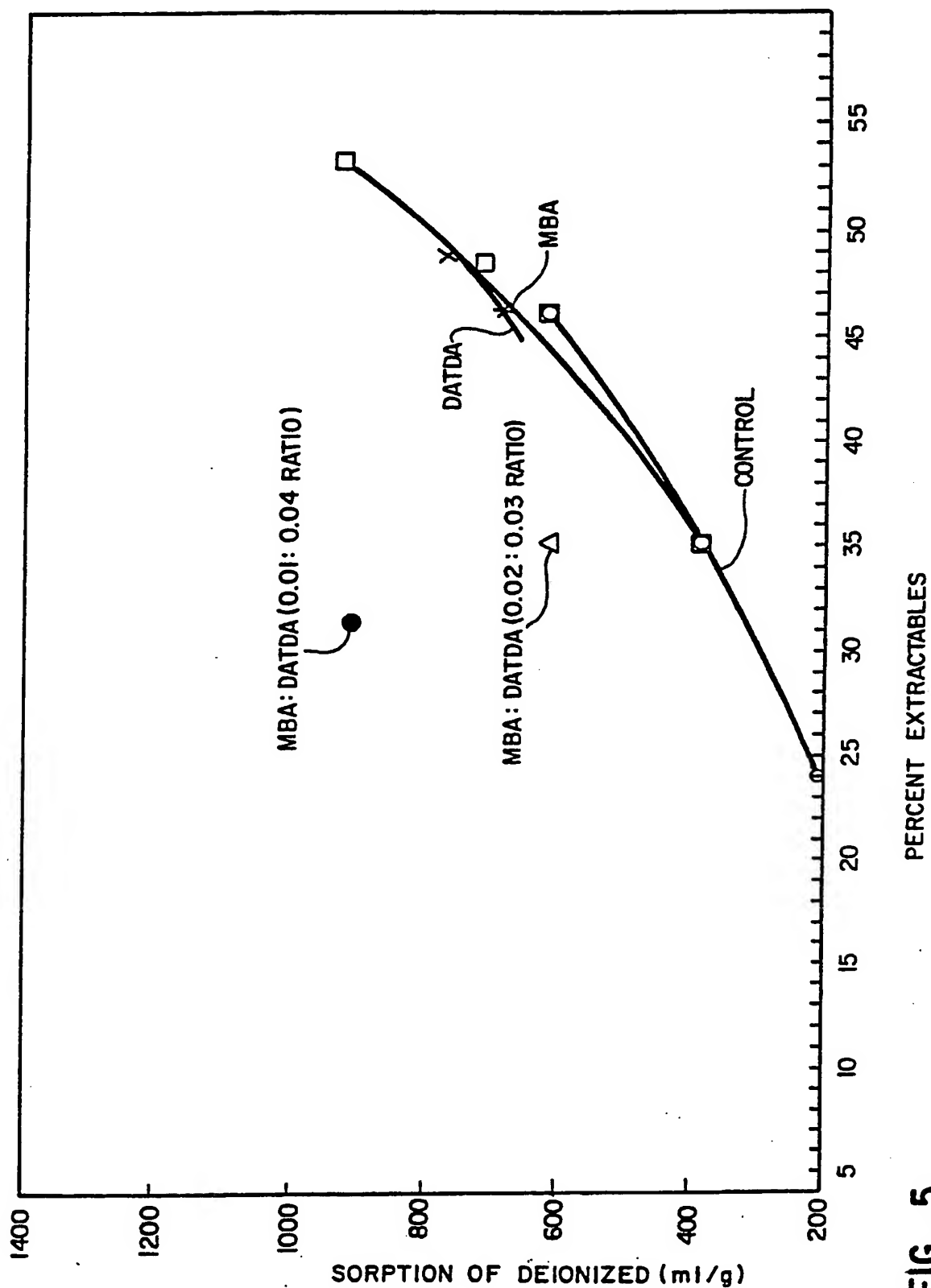


FIG. 4

SUBSTITUTE SHEET



PERCENT EXTRACTABLES

SORPTION OF DEIONIZED (ml/g)

FIG. 5

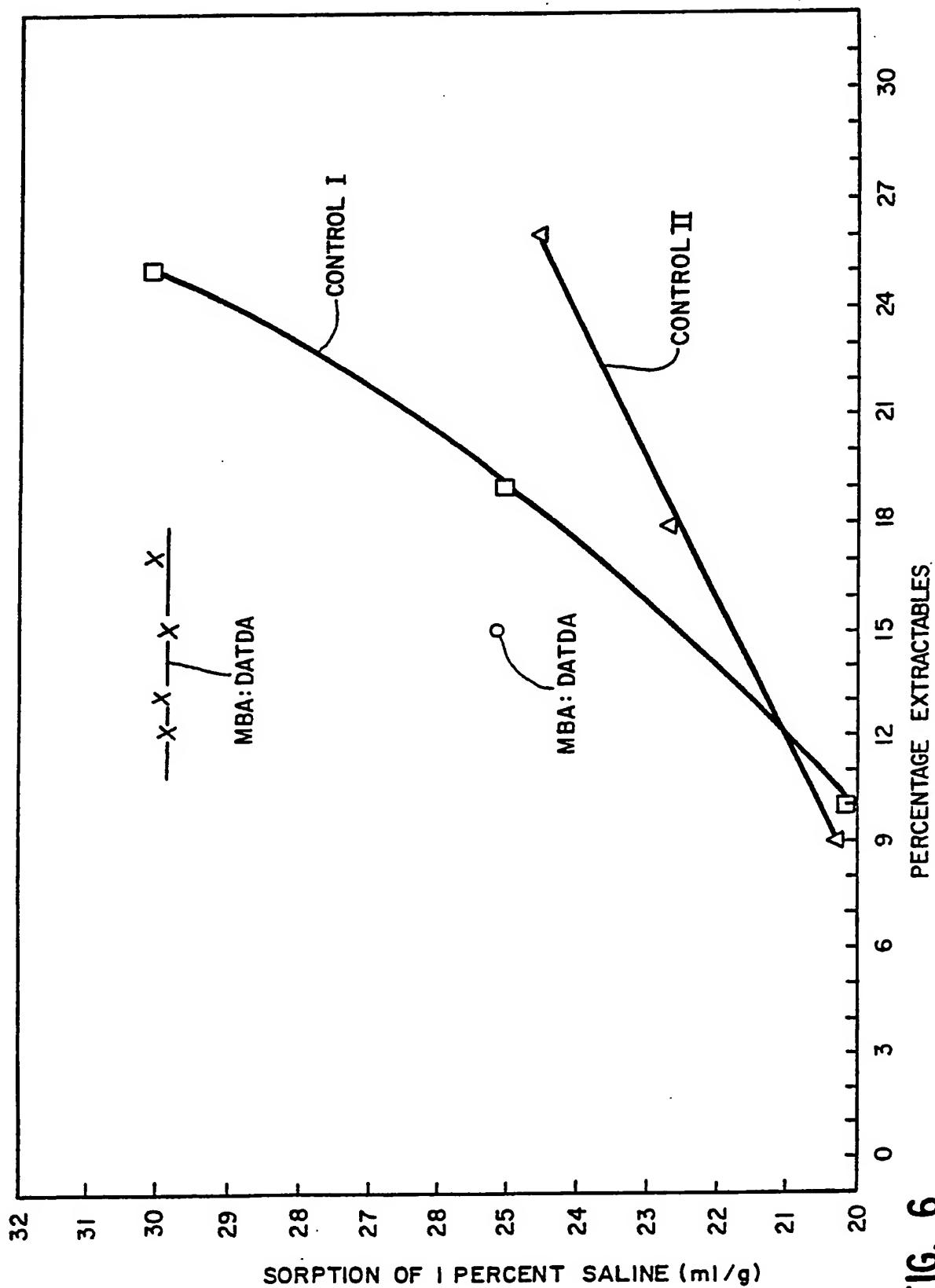


FIG. 6

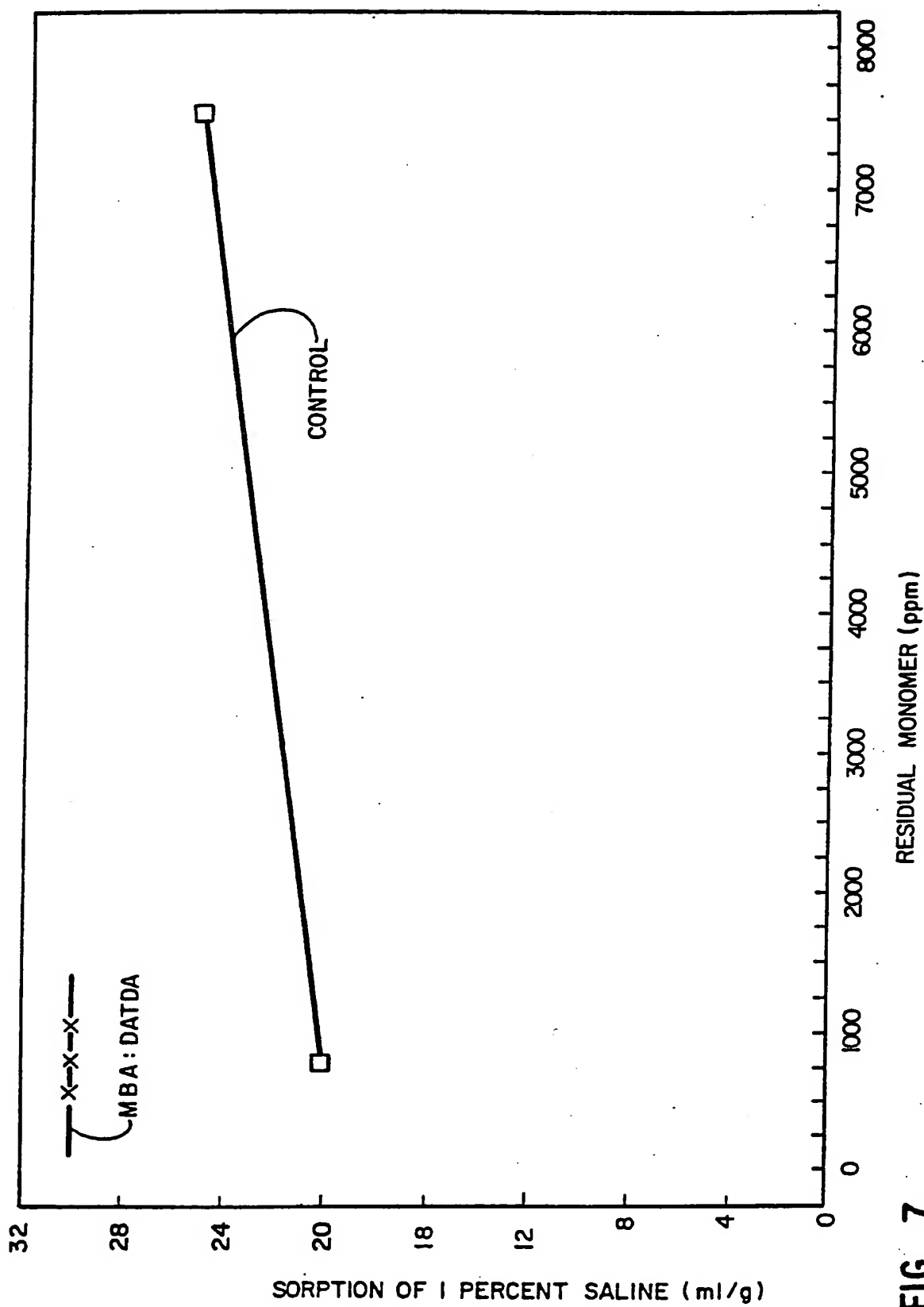
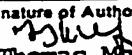
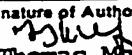
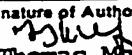


FIG. 7

INTERNATIONAL SEARCH REPORT

PCT/US90/03304

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08F 226/02, 236/02, 236/22; B32B 27/00, 27/20, 27/38; D04H 1/64 U.S. CL. 526/307.2; 428/286, 284, 289 290														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; padding: 5px;">Classification System</th> <th style="border: 1px solid black; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 10px;">U.S.</td> <td style="border: 1px solid black; padding: 10px;">526/307.2, 287, 265; 428/286, 284, 289, 290</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	526/307.2, 287, 265; 428/286, 284, 289, 290								
Classification System	Classification Symbols													
U.S.	526/307.2, 287, 265; 428/286, 284, 289, 290													
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 5px;">Category ⁹</th> <th style="width: 60%; border: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;"> <div style="text-align: center;">X Y</div> </td> <td style="border: 1px solid black; padding: 5px;"> US, A, 4,742,135 (SCHULZ ET AL) 03 MAY 1988 See the entire document. </td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;"> <div style="text-align: center;">1-8 9-21</div> </td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y,P</td> <td style="border: 1px solid black; padding: 5px;"> US, A, 4,929,494 (MATSUI ET AL) 29 MAY 1990 See the entire document. </td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">19-21</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y,P</td> <td style="border: 1px solid black; padding: 5px;"> US, A, 4,929,495 (STANISLAWCZYK) 29 MAY 1990 See the entire document. </td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">9-18</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	<div style="text-align: center;">X Y</div>	US, A, 4,742,135 (SCHULZ ET AL) 03 MAY 1988 See the entire document.	<div style="text-align: center;">1-8 9-21</div>	Y,P	US, A, 4,929,494 (MATSUI ET AL) 29 MAY 1990 See the entire document.	19-21	Y,P	US, A, 4,929,495 (STANISLAWCZYK) 29 MAY 1990 See the entire document.	9-18
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³												
<div style="text-align: center;">X Y</div>	US, A, 4,742,135 (SCHULZ ET AL) 03 MAY 1988 See the entire document.	<div style="text-align: center;">1-8 9-21</div>												
Y,P	US, A, 4,929,494 (MATSUI ET AL) 29 MAY 1990 See the entire document.	19-21												
Y,P	US, A, 4,929,495 (STANISLAWCZYK) 29 MAY 1990 See the entire document.	9-18												
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">09 AUGUST 1990</div> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 OCT 1990</div> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;">  Thomas McDonald, Jr. </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">09 AUGUST 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 OCT 1990</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;">  Thomas McDonald, Jr. </div>								
Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">09 AUGUST 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 OCT 1990</div>													
International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;">  Thomas McDonald, Jr. </div>													

FURTHER INFORMATION

CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING⁴

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-8, drawn to a water-swellaable polymer, Class 526, Subclass 307.2.
- II. Claims 9-18, drawn to a polymer coated web, Class 428, Subclass 290.
- III. Claims 19-21, drawn to a sorbent laminate, Class 428, Subclass 286.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. **Telephone Practice**
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

The international application lacks unity of invention under P.C.T. Rule 13 because of the following reasons:

Inventions I. and II. do not form a single inventive concept because they are related as mutually exclusive species in intermediate-final product relationship.

In the instant case, the intermediate product is deemed to be useful as components in desiccant compositions, and there is nothing on this record to show that the final product would be obvious in view of the intermediate product. Inventions I. and III. are related in the same manner.

Inventions II. and III. do not form a single inventive concept because they are related as mutually exclusive species in intermediate-final product relationship.

In the instant case, the intermediate product is deemed to be useful as a binder, and there is nothing on this record to show that the final product would be obvious in view of the intermediate product.